Industrial Liquid Discharge Treatment with Activated Carbon (Cap) Produced from Cocoa Pod Husk in Kampung Batik Laweyan Surakarta

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Abstract. The unit in the Kampung Batik Laweyan industrial area discharge significant quantities of liquid (industrial) discharge containing solvents, heavy metals, and suspended solids that are discharged into the sewerage system and/or the receiving environment without adequate treatment. Cocoa pod husk is a natural adsorbent and its existence is abundant in Surakarta, is cost effective. The use of powdered activated carbon (CAP) makes it possible to considerably reduce the concentrations of heavy metal pollutants contained in the effluents by its optimum adsorption capacity. The aim of this investigation is to study the adsorption of heavy metal (Cd) with CAP from cocoa pod husk. Activated carbon was prepared from cocoa pod husk, carbonized at 100°C in a muffle furnace for 4 hour and activated with 0.5 M NaOH by reflux method until 60°C for 24 hour. The resultant products were tested to adsorb the heavy metals in effluent water at varying contact time. The adsorption capacity and metal removal percentage was computed and recorded at the various varying parameters in the study; while the reaction attained equilibrium in 160 minutes contact time. The maximum Cd removal efficiency was 41.2% at a contact time of 100 minutes, Functional groups involved in biosorption of Ni (II) ions by coccoa pod husk (*Theobroma cacao*) is a group -OH and N-H. which reflects the importance of use of activated carbon in the treatment of industrial liquid discharges, including various treatment of batik industrial liquid discharge.

Keywords: Adsorbent, Cadmium, Cocoa pod husk, NaOH, Powdered activated carbon

1. Introduction

Technological development nowadays are driving faster in the industrial, transportation, household and even health sectors. Technological progress can have a negative impact in the form of environmental damage due to waste disposal. Wastes containing coloring compounds and various hydrocarbon compounds are often found as pollutants in industrial waste and exhaust gases which are generally sourced from dye plants, refineries, coloring and textile industries. Kampung Batik Laweyan has become one of the central and oldest batik industrial in Indonesia, hundreds of home until large-scale batik production houses operate in this region. In the process of batik industry in dying batik produces colored liquid waste and it contains heavy metals. Heavy metal polution is some of the consequences of the
industrial that has had detrimental impacts on human life, as well as the environment, The penetration of waste into rivers can be an environmental burden if there is no serious treatment.

The burden of batik production waste can be minimized by clustering waste using IPAL. Based on direct interviews with Laweyan people, in 2008 a part of the Batik industry was integrated in one place (IPAL Communal), but the deposited waste was only left to exceed the volume limit, the waste would still enter the river. Several industrial processes are sources of cadmium exposure to the environment as cadmium is used in electroplating, pigment, and paints manufacture [25][19]. Contamination of water sources due to exposure to heavy metals such as cadmium is a major problem from the indiscriminate release of chemical waste and effluents into water bodies.

Several alternative methods were developed to reduce heavy metal content from waste in order to minimize the environmental burden on aquatic ecosystems. Handling batik waste can be done in biology, chemistry or physics. Chemically it can be done by electrolysis, adsorption and coagulation [13][16]. Biologically by utilizing certain living things, for example by using algae and water hyacinth plants [7][9][22] and in physics using filtration [24].

One effort that can be done to deal with heavy metal wastes that pollute the river is by using bioadsorbent. Biosorbent is a material derived from natural materials and can be used to absorb chemicals contained in water bodies. It has a high surface area and porosity formed during the carbonization process so it has high adsorption ability [18]. There is a trend of active carbon production with agricultural byproducts in dealing with industrial waste. The skin of cocoa fruit (Theobroma cacao) is one of the ingredients that contains high cellulose. This waste residue is rich in lignocellulosic polysaccharides that have been reported to be responsible as adsorbents used in wastewater treatment [8].

In this study, activated carbon was obtained from cocoa agricultural waste in the Wonogiri area, the process stages included preparation of raw materials into activated carbon, characterizing and investigating the effectiveness of the adsorption of activated charcoal produced. The scope includes the production and evaluative efficiency of activated charcoal from Wonogiri cocoa peel in selective adsorption of Cd heavy metals in Laweyan's batik industrial wastewater.

2. Material

2.1. Adsorption

Adsorption is a natural process where molecules from dissolved compounds collect and attach to the surface of absorbent substances. Adsorption process takes place is called the adsorbate. Activated carbon is a part of a range of substances with a very high porosity and a significant surface area of the order of 500 to 1500 m² per gram of coal. These qualities give the activated carbon a high adsorption capacity. This high surface area allows the accumulation of large numbers of contaminant molecules [20]. Reeze [20] also said that adequate activation for useful applications may only originate from high surface areas, although further chemical treatments often improve the absorbing properties of materials.

Activated carbon has been produced from a large number of carbonated raw materials such as coal, wood, coconut shell and some agricultural waste products and animal sources. Activated carbon as an adsorbent is associated with a large surface area, universal adsorption effects, high surface reactivity and pore size [15]. Adsorption occurs in micropores and mesopores with micropore acting as a transportation channel. Carbon micropores are used in the gas phase process while mesoporous carbon is applied in the liquid phase process. In addition to their significant contribution to adsorption, mesopores also function as the main transport arteries for these adsorbates. Activated carbon is used to remove or isolate products from process or waste streams by adsorption [4].

2.2. Mechanism of Adsorption

Adsorbates are substance that concentrates at the surface of the pores. The adsorbents is a place that adsorption occurs. Mostly activated carbon is used as an adsorbent, it has many of pore structure that should have by adsorbent for transport of gaseous vapors. The basic principle of carbon adsorption is
the mass transfer and adsorption of a molecule from a liquid or gas into solid surface. Activated carbon has a porous structure that attracts and holds organic and inorganic molecules, as well as metals.

Harry et al. [12] said that adsorption of solutes to the interior surface of the adsorbent can take four steps: (1) Mass transportation: Adsorbates are transported around the particles of the adsorbent from the waste solution, (2) Transport films: Adsorbates are transported by molecular diffusion through a hydrodynamic layer of water that surrounds the particles of the adsorbent when water flows through it. The transport distance and absorption time of particles are determined by the flow rate passing through the particles; the higher the flow rate the shorter the distance, (3) Inter-particle transport: After the adsorbate passes through the hydrodynamic boundary layer, they are transported through the adsorbent pores to the available adsorption site. Intra-particle transport can occur by molecular diffusion through solution in the pores (pore diffusion), or by diffusion along the surface of the adsorbent (surface diffusion), then adsorption occurs [3][4]. (4) Adsorption of solutes at active sites: Adsorption bonds will be formed between adsorbates and adsorbents [1].

2.3. Cocoa (Theobroma cacao)

Many agriculture crops have physical properties which are essential for many others things. There are several reported that used cocoa as an adsorbent. Pandia [17] has determined the effectiveness of cocoa peel as adsorbents to reduce the content of COD in POME (Palm Oil Mill Effluent) and the results showed that particle size ≥120 mesh with adsorbent : HNO₃ ratio 1:4 produced the highest iodine number of 596.684 mg/g. The best adsorbent mass was 1 g at 2 h contact time with 56.79% removal percentage for COD.

Fabunmi [11] said that a cocoa pod shows a rough leathery rind about 3 cm thick. Filled with sweet (although not edible) slimy and pinkish pulp, enclosing from 30 to 50 large. Fabunmi, 2004 also said that investigated about physical properties of some agriculture crops that used for adsorbent materials, Cocos nucifera husk recorded have bulk density (0.0746 g/cm³), and ash content (3.95%), cellulose contents (0.52%). On the other hand, Theobroma cacao pods recorded the higher cellulose content (41.92%), ash content (12.67%), and crude fiber content (33.60%).

The cocoa plant is one of the plantation plants whose area of cultivation continues to increase. Increased planting area is followed by waste from cocoa fruit management. Cocoa fruit skin is the biggest waste produced, because it reaches 70% of the total fruit. Wonogiri district is one of the main cocoa producing areas in Central Java province. Based on BPS data (2018) Wonogiri Cocoa production reached 3,308 tons, interviews with residents in 2018, many of them just collected that seeds, while pod husk was left to become wasted materials. Because of its cellulose content, cocoa pods can be used as bioadsorbent of heavy metal cadmium and copper in the waters [14]. According to that report cocoa pod husk can be used in the production of activated carbon so that it can add intrinsic value to cocoa waste while recycling reset the waste.

2.4. Material and Method

2.4.1. Carbonization of cocoa pod husk. Carbonization or pyrolyzed is the process in which sample is heated, decomposed and eventually converted into desired product in the absence of air in a fixed bed reactor. Cocoa pod husk was firstly washed with water to remove dirt from its surface and subsequently dried at 80°C for 24 h to remove moisture. The dried cocoa pod husk was ground into small pieces and sieved with 100 mesh filter. The sample was kept in a plastic container and stored at room temperature.

2.4.2. Chemical activation process. The carbonized or pyrolyzed sample was sieved using 100 mesh size. Activation of the charred cocoa pod husk was carried out using the method employed by Badmus [6] with slight modification as follows: 100 g of charred sample was mixed with 100 mL of 1 M NaOH and refluxed by heating for 24 h. After slight cooling, the slurry was filtered, rinsed with diluted hydrochloric acid and dried at 60°C oven for 24 h. The dried sample was stored in airtight plastic container.
2.4.3. Making Cd\(^{2+}\) Standard Solutions. Making Cd\(^{2+}\) standard solution 1000 ppm is done by the method as follows: 3Cd(SO\(_4\))\(_2\).8H\(_2\)O weighed as much as 1 grams, then added HNO\(_3\) and crushed with aquabides to volume 1 L. Next, the standard solution Cd (II) 1000 ppm piped 100 mL and diluted to volume 1 L for make 100 ppm standard solution.

2.4.4. Optimum Time Determination Biosorption of Cd(II) Ion by Coccoa Pod Husk (Theobroma cacao). The effluent water sample was collected from the Premulung River. A 50 mL of the effluent water was collected and measured. Chocolate pod husk powder (Theobroma cacao) which is clean and dry are included respectively 1 grams agitated into 8 pieces erlenmeyer flask size of 100 mL and 50 mL of Cd(II) ion solution was added with a concentration of 100 ppm and shaken by using magnetic stirrer for 20, 40, 60, 80, 100, 120, 140 and 160 min. The pH adjustment of the solution was done using 1.0 M HCl or 1.0 M NaOH. Blank solutions were 42 filter paper, and analyzed for the residual concentration of metals in the filtrate by atomic absorption spectrophotometer (AAS), every experiment done in duplicate.

2.4.5. FT-IR Analysis. Bioadsorbent of coccoa pod husk (Theobroma cacao) before and after adding with Cd(II) solution with optimum pH and time and dried at 80 °C then analyzed by FT-IR (Fourier Transform Infrared) in area 4500-340 cm\(^{-1}\) with 1 cm\(^{-1}\) resolution at room temperature using DTGS detector (deuterated triglycine sulphate). The results of the mixture are put into a special place in a round shape and then mixed to release water.

2.5. Adsorption Experiment

For each experiment, 50 mL of effluent water sample containing mixed metals of 2.0 mg/L Cd, and pH of 7 was prepared based on effluent water metal concentration and added to a calculated amount of adsorbent (activated charcoal from cocoa pod husk) in 50 mL shake flask. The pH adjustment of the solution was done using 1.0 M HCl or 1.0 M NaOH. The adsorbent in solution was agitated in mechanical shaker at a speed of 1000 rpm at 60 °C. Blank solutions were treated similarly without the adsorbent and under control condition. The solution was filtered using a watchman 42 filter paper, and analyzed for the residual concentration of metals in the filtrate by atomic absorption spectrophotometer (AAS). The adsorption capacity of the adsorbent was calculated and recorded. Equilibrium contact time of metal at different adsorbent time (20, 40, 60, 80, 100, 120, 140, 160 min) at ambient temperature was used for computing the adsorption capacity and metal removal percentage (R\%). Also, equilibrium pH variation of metals was used to compute the adsorption capacity and removal percentage (R %).

3. Result and Discussion

3.1. Contact Time.

The optimum biosorption time of Cd (II) ions by coccoa pod husk (Theobroma cacao) was determined by calculating the number of Cd (II) ions which were adsorbed as a function of time. The relationship between contact time and the amount of Cd (II) ions adsorbed by brown fruit powder (Theobroma cacao) shown in Table 1.
Table 1 shows that the amount of adsorbed Cd (II) ions increased from the 20\textsuperscript{th} minute to the 100\textsuperscript{th} minute. After that the amount adsorbed tends to be constant and even decreases. Therefore, the 100 minute stirring time is optimum time obtained with the number of Cd (II) ions adsorbed at 0.842 ppm. This optimum time is used for research. Furthermore, the results of this study indicate that adsorption of Cd (II) ions by cocoa pod husk (Theobroma cacao) experienced an increase with the longer the contact time occurred between the adsorbent and the adsorbate but at a certain time (optimum time) the amount of Cd (II) ion adsorbed was maximal so that the number of Cd (II) ions adsorbed did not increase. The optimum biosorption time of Cd (II) ions in several other studies showed different results, depending on the type of biosorbent used.

Amaliah [5] in the study utilization of coral biomass as Bioadsorbent Cd (II) ions obtained the optimum time is 90 minutes. Optimum time difference on the biosorption process depends on content of compounds contained on the biosorbent surface. According to Setyawan [20] optimum time is the time to reach equilibrium that is when cluster the function of biosorbent is binding metal ions to the maximum and after the balance is reached the bond between active groups on the surface biosorbent and metal ions are weakened so the desorption process occurs. Interaction between functional groups at the surface of cocoa pod husk biosorbent with Cd(II) ions reaching conditions equilibrium at 100 minutes and after equilibrium conditions achieved the number of Cd (II) ions adsorbed decreases due to bonding between Cd (II) ions and functional groups on the surface of biosorbents increasingly weakened and finally released again into solution. Time that needed relatively fast because of the ion Cd (II) is chemically adsorbed forming a layer on the surface bioadsorbent.

### Table 1. Contact time of Cocoa Pod Husk Adsorbent Cd (II)

| Conc. Before (ppm) | Contact time | Adsorption Conc. (ppm) | % Cd (II) adsorption |
|-------------------|--------------|------------------------|---------------------|
| 2                 |              |                        |                     |
| 20 min            | 0.509        | 25.45                  |                     |
| 40 min            | 0.532        | 26.60                  |                     |
| 60 min            | 0.608        | 30.40                  |                     |
| 80 min            | 0.704        | 35.20                  |                     |
| 100 min           | 0.842        | 42.10                  |                     |
| 120 min           | 0.557        | 27.85                  |                     |
| 140 min           | 0.608        | 30.40                  |                     |
| 160 min           | 0.583        | 29.15                  |                     |

3.2. Results of Functional Groups

Infrared spectroscopy was used to obtain information on the nature and possible interactions between the functional groups on the bioadsorbent and the Cd (II) ion. Cocoa pod husk before adsorption and after adsorption analyzed using FTIR. Interaction between Cd (II) ions and skin Chocolate fruit (Theobroma cacao) shows in the spectrum of the reading IR spectroscopy Figure 1.
Figure 1. FTIR Results of Bioadsorbent Coccoa Pod Husk

Figure 1 shows that FTIR spectra from the cocoa pod husk (*Theobroma cacao*) before and after adsorption. Before adsorption several peaks appear, as in wave numbers 3421.87 cm\(^{-1}\) which is absorption from the -OH group. -OH Group is supported with the appearance of C-O uptake alcohol at wave number 1265.36 cm\(^{-1}\). N-H group from amine recorded at wavelength 1583.42 cm\(^{-1}\), this cluster is estimated derived from chocolate fruit peel protein which is reinforced by absorption 1737.86 cm\(^{-1}\) as absorption C = O (peptide bond). After adsorption there are several shifts in numbers wave. This can be seen in shift wave number from 3421.87 cm\(^{-1}\) to 3424.76 cm\(^{-1}\), which indicates the occurrence the interaction between the -OH group of biosorbent cocoa pod husk with ions Cd (II). This is also seen in shift wave number from 1597.13 cm\(^{-1}\) to 1583.83 cm\(^{-1}\) which indicates the occurrence biosorbent interaction with N-H groups. This proves that Cd (II) ions bound to the –OH and N-H. Shift also occurs in wave number of 575.88 cm\(^{-1}\) to 572.88 cm\(^{-1}\). This matter shows the absorption of bond vibrations Cd-O. Thing this is in accordance with the literature that vibration Cd metal with group O from ligand will appear in the wave number 600-400 cm\(^{-1}\) [23]. Based on shift wave number that occurs, then interaction is expected between Cd (II) with a hydroxyl group (-OH) from lignin and cellulose and Cd (II) with the N-H group from protein.

The cocoa pod husk adsorbent is lignocellulosic biomass, and these types of adsorbents which are composed of cellulose, lignin, and hemicellulose as major components have been reported as possible sites for complexation reactions with metallic cations during sorption. Ion-exchange is another mechanism that has been reported in literature as a mechanism of metal ion sorption.

A number of functional groups such as hydroxyl, sulfhydryl, sulfonate, carboxylate have been proposed to be responsible for sorption related metal ion binding in adsorbents. The ability of these groups also called active sites to bind metal ions during adsorption have been suggested by El-Kamash *et al* [10] to depend on a number of factor such as the quantity of sites, accessibility of sites, chemical state of sites, and affinity between metal ion and active sites [17]. For the cocoa pod husk adsorbent the data obtained from FTIR studies before and after Cd (II) sorption. Figure 2 shows that a number of
carbonyl (–CO), amina (–N–H) and hydroxyl (–O–H) groups may be active sites for metal ion interaction. These functional groups were observed to have decreased intensity or disappeared in the spectrum of the bioadsorbent after Cd (II) sorption.

4. Conclusion
A review of agricultural adsorbent from cacao pod husk presented here shows great potential for the elimination of heavy metal from wastewater. The sorption capacity is dependent on the type of the absorbent investigated and the nature of the effluent water. The use of commercially available activated carbon for removal of the heavy metal can be replaced by utilization of inexpensive, effective and readily available agricultural by-products as adsorbents. The adsorbent produced can be used effectively in the adsorption of heavy metals Cd2+ from effluent water. The removal of heavy metal was contact time for variation dependent as the adsorbent capacity and metal removal percentage increase with 100 mins contact time variation of the solution. As well as adsorption, ion-exchange is another mechanism that has been reported as a mechanism of metal ion sorption. Functional groups involved in biosorption of Cd (II) ions by cacao pod husk (Theobroma cacao) is a group -OH and N–H. From the results of the study it can be suggested: 1) Further research is needed to obtain a method of activation of cacao fruit skin adsorbent which is more effective using an activator solution other than NaOH and HCl solution, 2) research needs to be done to apply to heavy metals and other dyes that can adsorbed by the cacao pod husk adsorbent, and 3) further research is needed regarding the attributes of adsorbents with other variations, for example optimum pH and optimum mass of adsorbent.

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