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by Djamilah Arifiyana

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Optimization of pH and Contact Time Adsorption of Banana Peels as Adsorbent of Co(II) and Ni (II) from Liquid Solutions

Djamilah Arifiyana^{1,a)} and Vika Ayu Devianti^{1,b)}

¹Akademi Farmasi Surabaya, Surabaya, Jawa Timur, Indonesia

^{a)}djamilah.arifiyana@akfarsurabaya.ac.id

^{b)}vikaayu@akfarsurabaya.ac.id

Abstract. Co and Ni are heavy metals found in water and wastewater. Biosorption is a new treatment technology for handling heavy metal wastewater. Numerous studies have shown that many agricultural wastes have the ability to absorb heavy metal ions, such as banana peels. Therefore, the aim of this research were optimization of pH and contact time on the adsorption of Co(II) and Ni(II) by utilizing banana peels waste. The research began by making banana peels powder then characterizing using FT-IR to identify the functional group on banana peels powder. Determination of optimum pH was carried out at pH 3, 4, 5, 6, and 7 in 10, 20, 30, 40, dan 50 minutes contact time. The results of characterization showed that the presence of hydroxyl group at 3266 cm^{-1} and carboxylic acid (C=O) group at 1730 cm^{-1} . The optimum condition of Co(II) and Ni(II) adsorption at pH 4 with percentage adsorption were 34.74% (Co) and 41.43 (Ni); and optimum contact time in 30 minutes with percentage of Co(II) and Ni(II) adsorption were 36% and 25%, respectively.

INTRODUCTION

Co and Ni are metals produced from Industrial waste. Heavy metals in Industrial waste disposal has become a global problem because it can accumulate in the food chain and damage ecosystems and human health (1). Therefore, the presence of heavy metals in water and waste needs to be restricted.

There are many methods for handling heavy metal wastewater, for example by biosorption, ion exchange, solvent extraction, and membrane separation. Among these methods, adsorption by biomass (biosorption) is a new treatment technology for treating heavy metal wastewater and has very broad development prospects. Numerous studies have shown that many agricultural wastes have the ability to absorb heavy metal ions, such as banana peels (2). Banana as the highest consumption fruits in the world has a correlation with the waste produced. With abundant resources, environmentally friendly, and low cost, agricultural waste of banana peels can be converted into biosorbents so that they can be used to remove heavy metal ions in wastewater.

Banana peels contain organic compounds, such as cellulose that can absorb metal ions. The positively-charged metal ion will be bound by an electron-rich hydroxyl group. Banana peels can be used as good adsorbent for heavy metal adsorption (3). Biosorbent made from banana peels has been widely carried out in previous studies. Sirilert & Maikrang, (2018) (4) carried out adsorption of heavy metals (Pb and Cd) using banana peel biosorbents. Based on the results of this study, banana peels were able to adsorb Pb and Cd metals with an adsorption capacity of 2.6185 mg/g and 2.8810 mg/g . Wardani & Wulandari, (2018) (5) carried out adsorption of heavy metal Pb using banana peels biosorbents and obtained an adsorption capacity of 54.752 mg/g . Ali, (2017) (6) used banana peels as adsorbent and was able to adsorb Mn(II) until 94%. Arunakumara et al., (2013) (1) carried out heavy metal adsorption using banana peels biosorbents with an adsorption capacity of 7.97 and 5.80 mg/g .

Research on the adsorption of heavy metals Co and Ni on banana peels adsorbents and other biomass has not been widely carried out. Therefore, the aim of this study was to utilize banana peels waste which had the potential as an

adsorbent to adsorb heavy metals Co and Ni. Contact time and pH were optimized to obtain maximum adsorption capacity of Co and Ni.

MATERIALS AND METHODS

Adsorbent were made from banana peels. Banana peels used were Kepok banana peels (*Musa paradisiaca* L.) were obtained from household waste and fried banana traders in Surabaya, Indonesia. Functional group of adsorbent were analyzed using FTIR spectrophotometer. Adsorption was tested using Atomic Absorption Spectrophotometer (AAS).

Materials Preparation

Banana peels were cleaned from impurities then washed thoroughly. Banana peels were dried under the sun for 5 days then dried in oven at 70°C for 3 hours. The dried banana peels were blended and sieved using a 100 mesh sieve. The banana peels powder was then stored in an airtight bottle and 0.5 gram were taken to be analyzed for its functional groups using FTIR spectrometer.

Optimization of Contact Time Adsorption

Banana peels powder weighed 1.5 grams, then added 50 mL of 50 ppm Co solution. The pH of the test solution was adjusted to 6 by adding 0.1 M NaOH or 0.1 M HCl. After that, it was stirred using a magnetic stirrer at 240 rpm for 10, 20, 30, 40, and 50 minutes at room temperature. The filtrate obtained was then analyzed using Atomic Absorption Spectrophotometer (AAS) to determine the amount of Co (II) ions remaining in the solution while the resulting precipitate was determined for its functional groups using IR spectrophotometer. Same treatment was performed on Ni metal adsorption.

Optimization of pH Solution

Banana peels powder weighed 1.5 grams then added 50 ml of 50 ppm Co solution. The pH of the test solution was adjusted to 3, 4, 5, 6 and 7 by adding 0.1 M NaOH or 0.1 M HCl solution. Each mixture in the erlenmeyer was stirred using a magnetic stirrer at a speed of 240 rpm according to the optimum adsorption contact time (based on results of the optimization treatment contact time). The adsorption results were filtered and then the filtrate was analyzed using an Atomic Absorption Spectrophotometer to determine the amount of Co (II) ions remaining in the solution. While the resulting precipitate was analyzed for its functional groups using an IR spectrophotometer. Same treatment was performed on Ni metal adsorption.

Adsorption Studies

Each test solution were analyzed by Atomic Absorption Spectrophotometer. The adsorption percentage of Co and Ni metal ion adsorbed on banana peels were calculated by Eqs. :

$$\% \text{ Adsorption} = \frac{W_0 - W_1}{W_0} \times 100\% \quad (1)$$

Where W_0 and W_1 were the initial and final mass (g) of banana peels. All adsorption experiments were performed in triplicate and the mean values were used in data analysis.

RESULTS AND DISCUSSIONS

Banana peels used were Kepok banana peels (*Musa paradisiaca* L.). Kepok banana peels used were light yellow to dark yellow. Banana fruits were obtained from household waste and fried banana traders who used the basic ingredient of Kepok bananas. The method of preparing adsorbents were adopted from Anwar et al., (2010) (7). The banana peels waste was cut and then dried to reduce the moisture content contained in the banana peels. After that, it

was blended and sieved using a 100 mesh sieve to reduce particle size and increase the surface area of banana peels. The resulting banana peels powder was dark brown to black.

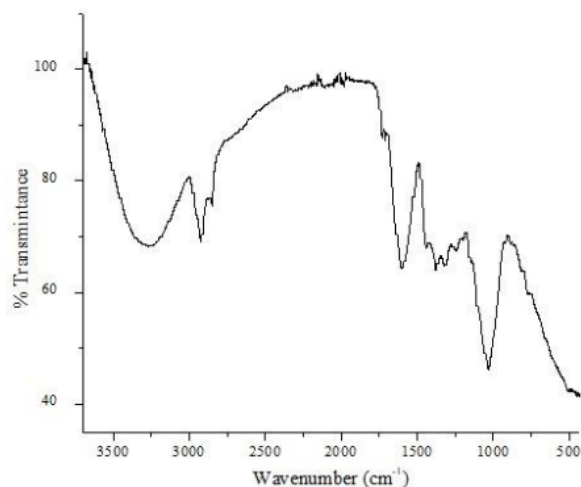


FIGURE 1. Spectrum FTIR of Polysaccharide Functional Group in Banana Peels

The functional groups of banana peels powder showed in Figure 1. The spectra that appeared at 3266 cm^{-1} indicated the presence of a hydroxyl group (-O-H), the spectra that appeared at 1730 cm^{-1} indicated the presence of a C=O group of carboxylic acids. These hydroxyl and carboxylic acid groups played an important role in the adsorption of Co^{2+} and Ni^{2+} ions. The bonding occurred between the metal ion and the -OH group on this polysaccharide was able to occur through hydrogen bonds and the van der Waals force. It led banana peels was utilized as biosorbent of heavy metals (8,9).

Effect of Contact Time

One of the important factors affecting metal adsorption was the contact time. The variations in contact time used for the adsorption of Co and Ni metals were 10, 20, 30, 40, and 50 minutes. The initial concentration of Co and Ni solutions were 50 ppm. Determination of contact time aimed to determine the minimum time required for the adsorbent to optimally adsorb cobalt (II) and nickel (II) metal ions until the same state was achieved between the adsorbed and released metals. Figure 2 showed the adsorption percentage which tended to be constant at the contact time of 10 and 20 minutes, then it increased from 11% to 25% and 30% to 36% in Ni^{2+} and Co^{2+} metals, respectively. The longer the contact time, the interaction between banana peel adsorbent and Ni^{2+} / Co^{2+} ions occurred effectively. This is because the active side of banana peel adsorbent were still able to bind metal ions effectively so that it can adsorb metal ion (I). After that, it decreased at 40 and 50 minutes. This indicated that banana peels adsorbent has been desorbed (releasing the metal ions that have been adsorbed) because banana peels adsorbent were saturated, all the active groups were bounded to metal ions so that it is unable to adsorb metal ions anymore (10). From Figure 2, it is shown that the optimum adsorption time of cobalt (II) and nickel (Ni) metal ions by banana peels powder was 30 minutes. The adsorption equilibrium occurred at 40 minutes. It was proven by the curve that tended to slope after 40th minute.

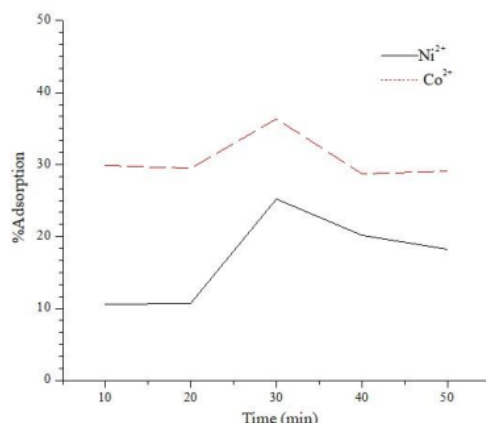


FIGURE 2. Optimization of contact time on adsorption of Ni²⁺ and Co²⁺ on Banana Peel

The absorption power in this study was smaller when compared to the results of the study by Abbasi et al., (2013) (2) who used banana peels to adsorb Co metal, where the optimum contact time occurred at 30 minutes with the adsorption percentage of 81%. It was because the banana peels powder in this study was not soaked with acid solvent so that there was only a few active sites involved in the adsorption process.

Effect of pH

pH was one of the parameters that affected the metal adsorption process due to the activity of functional groups on the adsorbent surface, the solubility of metal ions in solution, and the competition for metal ions in the adsorption process depending on pH conditions (9,11). Based on the graph in Figure 3, it showed that the adsorption percentage of Ni metal at pH 3 was 39% then it increased at pH 4 to 41% then decreased at pH 5 to 23% and increased again at pH 6 and 7 which was equal to 25% and 27%. The percentage of Ni²⁺ ions adsorbed on the adsorbent decreased at pH 5 due to the reduction of H⁺ ions in the solution so that the reduced deprotonization of functional groups on the adsorbent surface results in decreased binding ability (11,12). Adsorption of Ni²⁺ ions increased at pH 6 and 7 due to the reduction of competition between H⁺ ions in the solution and positively charged metal ions (Ni²⁺) on the adsorbent surface so that metal ions were able to be easily absorbed in the adsorbent. However, if the solution tended to be alkaline, hydroxy species such as Ni(OH)₂ and Co(OH)₂ would be sediment in the solution so that the decrease in metal ion levels was not only affected by the adsorption process but also by the deposition process (13,14).

According to Annadurai et al., (2003), (15) the adsorption process was able to run at pH > 2. Annadurai et al., (2003) (15) added that the more alkaline a metal solution system was, the metal would be bounded by OH⁻ to form a precipitate. The adsorption percentage of metal Co at pH 3 and 4 tended to be constant, namely 35.07% and 34.75%, then there was a decrease in percentage adsorption at pH 5, 6 and 7 of 19.769%, 22.366% and 25.210% respectively. Thus, pH 4 was chosen as the optimal pH because it referred to research conducted by Al-Shahrani et al., (2018) and Khamidah et al., (2011) (16,17) who showed that pH 4 was the optimal pH in the adsorption process of metal Co.

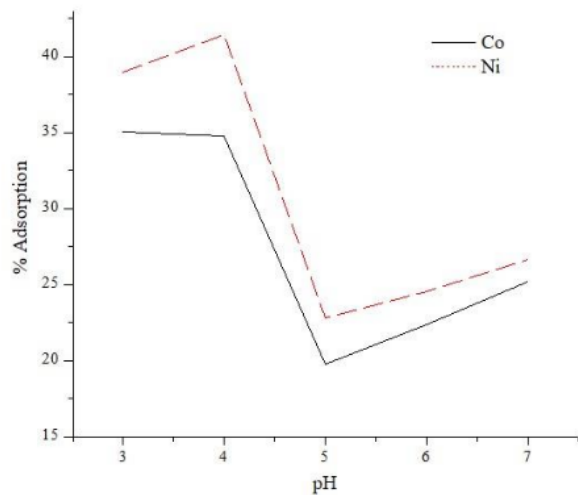


FIGURE 3. Optimization of on adsorption of Co^{2+} dan Ni^{2+} on Banana Peels

CONCLUSION

Based on the research that had been done, it was concluded that the results of adsorption of Ni and Co metals using optimum Kepok banana peels at 30 minutes of contact time with adsorption percentage, respectively, were 25% and 36%. Meanwhile, the optimum adsorption percentage of Ni and Co occurred at solution pH 4 with adsorption percentage, respectively 41.43% and 34.74%.

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