Neutron activation analysis of natural dyes elements to minimize batik industry wastewater

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Abstract. The improvement of the batik industry besides having a positive influence on improving the economy and the welfare of the community also has negative impacts. One of the negative impacts is the emergence of batik industry waste water in quite large quantities. Therefore the use of natural dyes is seen as an alternative effort in terms of minimizing the quantity of batik waste. The batik production process involves heavy metal elements so that the waste also contains heavy metal elements which can potentially pollute the environment. Some batik industries in Yogyakarta do not yet have a waste treatment plant so that the waste is directly discharged into the environment. In this study an analysis of heavy metal elements contained in natural dyes are Tegeran (Cudrania Javanensis) and Jalawe (Terminalia bellirica) by the neutron activation analysis method and enumeration was carried out using a spectrometry detector conducted at Centre of Science and Accelerator Technology-Yogyakarta. This Research state that some metal element Tegeran (Cudrania Javanensis are Th$^{227}$, Gd$^{161}$, Kr$^{88}$, Na$^{24}$, I$^{135}$ dan K$^{40}$. While Metal elemen in Jalawe (Terminalia bellirica) are Th$^{227}$, Rh$^{104}$ ,Ir$^{192}$, Br$^{84}$, Tl$^{208}$, I$^{135}$, Eu$^{152}$, I$^{134}$, Y$^{92}$ dan K$^{40}$. The use of natural dyes with optimal fixation will produce different color variations. This is because the bonding of metal elements with each metal type in the fixator will form different chemical bonds. It is hoped that by analyzing the metal content of natural dyes, batik performers can use natural dyes optimally and can minimalize wastewater in batik industry.
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1. Introduction
Enhancement of demand for batik products, it also followed the diversity of consumer tastes towards the color of batik. This makes the batik industry must develop color variations in its products. Technological advancements are able to create synthetic dyes for the batik industry with a variety of color variations. Synthetic dyes have several advantages, among others, easily available in the market, guaranteed color availability, various colors and is more practical and easier to use [1], [2] and more economical [3] and cheaper [2], [4]. In addition, synthetic dyes are more stable, resistant to various environmental conditions, have a stronger color and have a wider color range [2] and are not easily faded and are brightly colored [5].

The use of azo dyes is still widely used in the batik industry because the price is economical, easy to obtain, has a wide and varied color range and has the advantage of producing bright colors compared to other synthetic colors. But since August 1, 1996, developed countries such as Germany and the Netherlands have banned the use of synthetic dyes containing diazo salt. This prohibition refers to CBI (Center for the promotion of imports from developing countries) Reference CBI / NB-
3032 dated June 13, 1996 concerning dyes for clothing, footwear, bed linen may not use dyes that contain chemicals (synthetic). Waste from synthetic dyes is considered to have a serious impact on the environment including heavy metals and mutagenic intermediate dyes. The metal content, including: Cu, Ni, Cr, Hg and Co [6].

Based on characteristics of the synthetic dyes mentioned above, the waste has the potential to cause environmental pollution and is a toxic hazardous material, because some elements in synthetic dyes can be degraded into carcinogenic and toxic compounds [5], [7]. Furthermore [5] states that the textile industry waste includes colorful batik and chemicals from synthetic dyes. Mixing colloidal material with dye waste can increase turbidity and make water look bad, smell bad, prevent sunlight penetration. The impact is the depletion of dissolved oxygen, decreased water quality and the death of living creatures that live in it due to lack of oxygen or contaminated with toxic compounds [7]. In addition, when the waste is allowed to flow it will clog the pores of the soil which results in loss of soil productivity, hardened soil texture and prevents penetration of plant roots [5].

Natural dyes are alternatives to dyes that are non-toxic, renewable, easily degraded and environmentally friendly [8]. This makes the majority of batik industry players, looking for other alternatives by switching from the use of synthetic dyes into natural dyes that have become a heritage of ancestors. Natural dyes come from plants that have different shapes and levels, this is influenced by factors such as climate, soil, age, and other factors. Natural dyes commonly used by batik include colors obtained from Tegeran plants (Cudrania javanensis) and Jalawe (Terminalia bellirica). But in the process of batik production, namely the process of natural dyes dyeing in general have weaknesses that are fast fading, less sharp and the dyeing process requires a relatively long time and must be repeated. Natural dyes have a very natural color effect, low pigment concentration, low pigment stability, not as broad spectrum of colors as synthetic dyes. So there needs to be treatment so that natural dyes can have adequate quality such as synthetic dyes.

To make natural dyes stronger and sharper the fixation process can be done, namely the generation of natural dyes (color lock) because it functions to bind the colors into batik cloth. Fixation is a process to strengthen colors so they do not fade easily. Fixation can be done with several materials such as: alum, lime or tunjung. Each fixator has different characteristics of color. Fixation is a process that is carried out after dyeing, the purpose is to neutralize and generate dyes that have entered into the fiber of batik cloth, with color fixation will not or difficult to return after the natural dyes enter the fiber. So fixation is the process of locking the dye after the dyeing process so that the color that has seeped into the fiber does not fade easily and becomes sharper. Dyes which are directly dyed (dye) are generally low fastness, especially not resistant when washing. The fixation process makes better fastness and can be used to improve color quality. Fixation is done after the cloth is dyed and dry.

According to the original fixator is classified into two, namely synthetic fixators and natural fixators. Synthetic fixators come from materials undergoing synthesis and are mixed with elements of chemical compounds such as tunjung (FeSO₄), alum carbonate or soda ash (Na₂CO₃). Whereas natural fixators derived from natural ingredients that are processed naturally, for example: lime, lime, palm sugar, molasses, bananas and cashew nuts. How to use chalk fixers and tunjung is also different. Lime is a synthetic fixator obtained from heating limestone formed oxides of calcium or magnesium. In this process water reacts and is bound by CaO to Ca(OH)₂ with the same number of molecules. Lime in its use is dissolved first with a ratio of 20 grams of lime in each liter of water used, then precipitated and taken a clear solution then the cloth that has been inserted into the dye is put into batik cloth that has been done coloring. While the fixation fixation solution is done by dissolving 50 grams of tunjung in each liter of water used and let it settle, take the clear solution.

High awareness of batik industry players to use natural dyes not only to explore variations in various plants but also have a positive impact on the environment so as to reduce the volume of wastewater. Along with the increasing use of natural dyes among batik industry players it is unfortunate that in general it is still limited and the lack of knowledge about the content of elements especially the metallic elements in batik natural dyes. Therefore, it is considered very important to
carry out continuous research on the source of natural dyes and the element content contained in these natural dyes.

In this research, elements analysis was carried out on 2 (two) types of batik natural dyes, especially for Tegeran (Cudrania javanensis) and Jalawe (Terminalia bellirica) dyes by the Neutron Activation Analysis (NAA) method conducted at the Center of Science and Accelerator Technology-Yogyakarta. The results of this study are expected to be beneficial for the batik industry and researchers in the world of batik and textiles for the development of the batik industry.

2. Methodology

2.1. Tool
In this study the tools used include: sample preparation tools, irradiation tools, and counting tools.

2.1.1. Sample preparation tool. The sample preparation tool is the equipment used to dissolve batik natural dyes.

2.1.2. Sample preparation steps. There are four steps: Handy step to insert samples into a polyethylene vial, polyethylene vials as a place for liquid waste used during activation or counting, plastic clips to place polyethylene vials during activation, and cladding as a vial for polyethylene during activation.

2.1.3. Irradiation Tool. The irradiation was carried out at the Kartini Reactor by Center of Science and Accelerator Technology -Yogyakarta.

2.1.4. Counting Tool. The instrument used in this study uses a gamma spectrometer: NaI detector (Tl) performed under the following working conditions Quartz Type 12512/3 A-Dz 393, Voltage 600 V Canberra 3002, Pre Amp 100V Ortec 311, Dual Channel Analyzer (Multi Channel analyzer / MCA) 7010.

2.2. Materials
The research materials used in the study were 2 (two) types of batik natural dyes, especially for natural dyes namely Tegeran (Cudrania javanensis) and Jalawe (Terminalia bellirica). Extraction is the process of making a solution of natural dyes for taking color generating pigments found in plants, whether found in leaves, stems, roots, fruits, seeds, or flowers [9]. Extraction process by boiling the material using water. Extraction is intended to obtain dyes from plants so that dyes can be used as batik dyes. In this study a comparison of 1: 7 means 1 kg of Tegeran (Cudrania javanensis) or Jalawe (Terminalia bellirica) plants with 7 liters of water.

2.3. Method
2.3.1. Procedure for preparing natural dye samples. Samples of natural dye samples were each taken 50 ml, filtered with filter paper and then put into a measuring flask. Before concentrated this water sample is added with 5 ml of HNO₃ as strong acid until the color of the sample changes slightly brightly; this HNO₃ serves to damage the bonds of organic compounds that bind the metal and dissolve the metal. Then the sample is heated with an electric stove until the volume becomes 150 ml. Concentration results are taken with a pipette of 1 ml, then put into a vial polyethylene. After this stage the water sample is ready to be irradiated.

2.3.2. Irradiation. Irradiation is carried out, approximately for 6 hours. At the beginning of the appointment the radiation exposure measurements were taken and a result of 31.5 mR was obtained, the results were still relatively high so the samples had to be left to reduce the radiation exposure. The snippet is left for 322 hours, 50 minutes, 12 seconds. In addition to reducing radiation exposure, this phase is also to remove impurities that have been activated.
2.3.3. **Counting.** After irradiation is complete, the sample is chopped using a romet spectrometer. Determination of isotopes by qualitative analysis and quantitative analysis is based on analysis of the energy spectrum - $\gamma$ emitted by radioisotopes.

3. **Result and Discussion**

3.1. **Result**

Neutron Activation Analysis Method (NAA) is an analytical method that utilizes the principle of the reactivation reactor of an element with neutrons, both fast neutrons and thermal neutrons, which will emit radiation $\gamma$ with the specific energy that characterizes the element, while the radioactivity emitted from the reactivation element it will be proportional to the content of the analyzed elements [10]. Radioactivity is a spontaneous change in the state of the atomic nucleus accompanied by radiation in the form of particles and or electromagnetic waves. This phenomenon essentially shows the instability of the nucleus.

The comparison of the count of neutrons and protons in a nucleus determines the stability of the nucleus, in other words can determine whether the nucleus is radioactive or not [11]. Radioactive decay or disintegration is a change in the nucleus of an atom will bring a change from one nuclide to another nuclide or from one element to another [12]. The number of nuclei of N at time t is expressed in the radioactive constant per unit time $\lambda$ according to equation 1. And the number of parent nuclei before decay is $N_0$ at time $t = 0$ [13]

$$N_t = N_0 e^{-\lambda t}$$

where:
- $N_0$ as the initial amount of radionuclides or counts of the parent nucleus at $t = 0$,
- $N_t$ as the number of radionuclides or counts of parent nuclei at time t,
- $\lambda$ as the decay constant,
- e as a natural number whose value is equal to 2.71828, and,
- t as the decay time in seconds.

The events of neutron interactions with atomic nuclei can be described in terms of cross-sectional concepts. The latitude of a reaction is the probability of a neutron that will react with the nucleus. These latitudes are influenced by the speed of neutrons, the type of nucleus and the density of the nucleus. Neutrons which hit the nucleus of the atom and pulverized material always move, then with a fast neutron movement will have a narrow cross-section of the nucleus [14].

Each material has a different cross-section and threshold energy, so that exposure to particle-\(\gamma\) arising from each nucleus that reacts with neutrons becomes different. Therefore the result of exposure to radioactive particles emitted will be directly proportional to the neutron flux density and the cross-section of the material [11]. Spectrometer is an electronic device used for spectrum analysis – of a radioactive sample being measured. The output is in the form of a high-distribution pulse of the power spectrum absorbed by the detector, then processed on an electronic device causing a pulse count.

From these chopped pulses it can be seen the radioactive content contained in heavy metals. Spectrometric analysis for the identification of elements is carried out qualitatively through the power of light - emitted for radioactivity in the sample. This – ray energy is very characteristic for each radionuclide. After the power is calculated, it is then matched with an isotope table from [15] to determine the radioisotope contained in the sample. The sample to be analyzed is irradiated using a neutron source and the reaction (n, $\gamma$) Y will occur. The nucleus of the elements in the sample will capture neutrons and turn radioactive. Furthermore, after neutron radiation exposure is considered sufficient, the sample is removed from the neutron source. The footage now contains elements that emit radioactive rays. $\Gamma$ rays emitted by various elements in the sample can be analyzed by spectrometry $\gamma$. Qualitative analysis is based on the determination of tenaga ray energy, while
quantitative analysis is carried out by determining its intensity. If stable elements such as heavy metals in the sample are activated with neutrons, the most frequent and most widely used reactions are [16]:

\[ z \cdot XA + 0 \cdot n_1 \rightarrow z \cdot XA + 1 + 0 \cdot \gamma_1 \]  

(2)

where:
- \( Z \) is the atomic number,
- \( A \) is the mass number,
- \( X \) indicates heavy metals in stable condition,
- \( 0 \cdot n_1 \) is the operational symbol of a neutron, and
- \( \gamma \) is a symbol for gamma rays.

The reaction in equation (2) is called a neutron activation reaction that can be used for the NAA method. The emergence of radioactivity induced from a sample after neutron fire is a basic principle of NAA. The results of activation in reaction (2) are radioactive isotopes that emit light - with specific energy. In interactions with neutrons, neutron flux density is known. Neutron flux density is the number of neutrons that penetrate the collection of samples each time unit at a certain area, neutron flux density symbolized \( \Phi \), which depends on neutron density and neutron speed [14].

The pulse height produced by the HPG detector at spectrometry-\( \gamma \) is equivalent to the energy of the \( \gamma \) ray that hits the detector. The number of pulses that have a height is recorded in a channel with a certain channel number. Thus the double channel analyzer number is also proportional to the \( \gamma \)-ray energy. For a spectrometer device \( \gamma \) and a working condition setting, it is necessary to know the correlation between the channel number and the energy level. This can be done by chopping up a number of standard radioactive sources. When a plot of the photon-energy energy level versus a channel number is drawn, a straight line is obtained. The plot is called power calibration. According to Debertin who was adapted in [17] efficiency in experimental physics is defined as the ratio between the response of a measurement instrument (e.g., scale reader, electric current, number of counts) with the measured physical quantity value.

In spectrometry, physical quantities measured are the total count rate or photoelectric peak count and photon-energy energy level. In spectrometry counting, with enumeration aimed at one of the energy of the many energies and decay modes that exist in the trailer, then the efficiency of enumeration is based on the ratio between the count rate, activity, and absolute intensity values. In spectrometry -\( \gamma \) detector efficiency values can be obtained in two ways, namely through the calculation of geometry (absolute method) and relative methods, i.e., comparing the sample to be sought with the standard material whose levels are known, or through enumeration of a standard source of known activity. But the latter method is more accurate so it is more widely used [10].

Table 1. Qualitative analysis result for natural dyes Tegeran (Cudrania Javanensis).

| Energi (KeV) | Element   |
|-------------|-----------|
| 85.29       | Th-227    |
| 101.40      | Gd-161    |
| 361.81      | Kr-88     |
| 5168.29     | Na-24     |
| 3673.50     | I-135     |
| 1460.83     | K-40      |

Qualitative analysis was carried out to determine the types of elements contained in 2 (two) natural dyes, namely Tegeran (Cudrania javanensis) and Jalawe (Terminalia bellirica) solutions. Data
analysis was performed after counting data was obtained using spectrometry-γ. From the counting sample, data obtained in the form of energy spectrum -γ. Based on the energy spectrum muncul arising from the results of the counting sample, then further qualitative and quantitative analyzes are performed. Qualitative analysis is done by determining the peaks in the gamma energy spectrum. After the peaks in the energy spectrum are determined, then matched with the Neutron Activation Table, the types of elements contained in the Tegeran (Cudrania javanensis) and Jalawe (Terminalia bellirica) solutions can be identified. Qualitative data on the types of elements contained in 2 (two) natural dyes, namely Tegeran (Cudrania javanensis) and Jalawe (Terminalia bellirica) with the activation of the decay time and the long life decay time are shown in table 3.

Table 2. Qualitative analysis result for natural dyes Jalawe (Terminalia bellirica).

| Energy (KeV) | Element |
|-------------|---------|
| 286.86      | Th-227  |
| 556.25      | Rh-104  |
| 612.01      | Ir-192  |
| 802.96      | Br-84   |
| 859.59      | Ti-208  |
| 1100.91     | I-135   |
| 1111.50     | Eu-152  |
| 1136.55     | I-134   |
| 1404.51     | Y-92    |
| 1460.95     | K-40    |

3.2. Discussion

The dyeing process of batik with Tegeran (Cudrania Javanensis) and Jalawe (Terminalia bellirica) dyes is carried out at room temperature. Natural dyes are not completely absorbed, so that some others only stick to the surface of the fabric [18]. Fabric fibers do not bind the entire dye that is absorbed, so that the rest fade in the process of removing batik wax. In the process of releasing the batik wax using hot water and soda ash as auxiliary substances that are alkaline, so the intensity of the color of batik cloth has decreased. The initial concentration of natural dyes is influenced by the chromophore content in the source of natural dyes and the extraction conditions namely the type of solvent and the extraction temperature. One of the compounds extracted from Tegeran (Cudrania Javanensis) and Jalawe (Terminalia Bellirica) is tannin. Extracted tannins are often mixed with a mixture of phenolic and non-phenolic complexes (polysaccharides and proteins) [19], so as to reduce the potential of natural dyes absorbed into the fabric. High concentrations of natural dyes provide higher color aging and reduce the frequency of batik dyeing.

NAA with Kartini Reactor at Center For Science and Accleratror Technology irradiation can be applied to analyze elements in various physical forms (solids, liquids and gases), besides that it can also be used to find out how much element content in a sample. From the results of the spectrometer counting by looking at the peak of the energy spectrum to find out the heavy metal elements in natural dyes namely Tegeran (Cudrania Javanensis) presented in table 1. Tegeran (Cudrania Javanensis) contains the metal element Th-227, Gd-161, Kr-88 , Na-24, I-135 and K-40. Whereas Jalawe (Terminalia Bellirica) contains metal elements. Weights Th-227, Rh-104, Ir-192, Br-84, Ti-208, I-135, Eu-152, I-134, Y-92 and K-40. In this study quantitative analysis cannot be done to determine the calculation of the metal element content in the two natural dyes because of the limitations of standard natural dyes as a standard comparison value.

One of the important things that determines the color direction of the color of cotton batik industry is the type of fixation material used. From the results of the coloring that have been done on the dyes from Tegeran (Cudrania Javanensis) and Jalawe (Terminalia Bellirica) materials with alum fixation,
chalk is not too significant the difference in color will be more noticeable when used fabric tunjung fixation materials look darker when compared to the results of alum fixation. fixation with alum and lime. In staining with Jalawe (Terminalia Bellirica) the resulting color is brown with alum fixation, if the lime material fixation is used the color will turn lighter to light brown. When the fixation is used, the color will turn dark brown, the difference from the previous color is quite obvious. Of the three alum fixation, chalk and tunjung color is almost the same only in fixation with a darker brown tunjung color.

The most noticeable color change resulting from the three binding agents (fixation) is the use of tunjung. This is due to the reaction between tannins and Fe$_{2}^{3+}$ metal which produces complex salts (ferro tanate) so that it produces a black color when the process of dipping fabric into fixation materials. The potential of natural resources in Indonesia is very much so that it will support the exploration of making natural dyes which is preferred because of its superiority in terms of environmentally friendly, has a very special and unique color that is produced so that it will have a high sale value.

The fixation process is carried out with the aim to tie the colors to the fabric so that the colors remain attached to the fabric and maintain the stability of the coloring results obtained from the coloring process. In the fixation process is done by dipping the cloth that has been colored in a solution of tunjung (FeSO$_4$), alum KAl (SO4)$_2$12H$_2$O, or lime tohor (CaCO$_3$). If viewed from the material used in the fixation process, naturally the color is not environmentally friendly enough in the process of making batik because there are heavy metal elements used in the process, namely FeSO$_4$. The use of Aluminum (Al) and Iron (Fe) metals in the process of making batik is not only in the fixation process but also in the material preparation process (mordanting). The addition of these two elements is often used to speed up the process of opening the pores in the fabric fibers so that the dye can be absorbed on the fabric.

4. Conclusion
From the results of this study it can be concluded that:

a. Neutron Activation Method can be used to analyze heavy metal elements in natural dyes qualitatively.
b. The heavy metal content in Tegeran (Cudrania Javanensis) contains metal elements Th-227, Gd-161, Kr-88, Na-24, I-135 and K-40
c. Jalawe (Terminalia bellirica) heavy metal content contains heavy metal elements Th-227, Rh-104, Ir-192, Br-84, Tl-208, I-135, Eu-152, I-134, Y-92 and K-40
d. The use of natural dyes with optimal fixation will produce different color variations. This is because the bonding of metal elements with each metal type in the fixator will form different chemical bonds.
e. The use of natural colors, especially Tegeran (Cudrania Javanensis) and Jalawe (Terminalia bellirica) can minimize liquid waste because the use of natural colors can be done repeatedly (refill color).

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