Rosa sp and Hibiscus sabdariffa L extract in ethanol fraction as acid base indicator: Application of green chemistry in education

M Paristiowati1*, M Moersilah1, M M Stephanie3, Z Zulmanelis1, R Idroes2 and R A Puspita1

1Department of Chemistry Education, Universitas Negeri Jakarta, Jakarta, Indonesia
2Department of Chemistry, Syiah Kuala University, Banda Aceh, Indonesia
3Magister Program, Department of Chemistry Education, Universitas Negeri Jakarta, Jakarta, Indonesia

*maria.paristiowati@unj.ac.id

Abstract. Green Chemistry principal was introduced in an academic environment in the 1980s as guidelines for sustainable development focused on chemistry. Efforts to realize these expectations can be applied through education by developing learning process based on environmental. This study aims to apply the concept of Green Chemistry in education, especially chemistry learning by producing natural acid-base indicators from the extract of roses (Rosa sp) and Rosella (Hibiscus sabdariffa L). These indicators are produced by the method of extraction using 96% ethanol solvent in an acidic atmosphere at pH 3-4. The results of maceration then extracted in three different solvents (ethanol, n-hexane, and chloroform). The extract was tested in solution with pH 1-12 and used as an indicator to identify the solutions and titration in acid-base topic. It concluded that the roses and Rosella can be used as an alternative raw material for acid base indicator. The use of roses and Rosella indicates an attempt to have applied the principles of green chemistry, including the prevention of the formation of hazardous wastes, the design of safe chemical products, the use of renewable materials, the design of materials that are easily degraded, and the use of safe solvents.

1. Introduction
The rapid development of science and technology into the 21st century is currently affecting many aspects in life. Education is one of the important aspects that involved. In recent years, experts in science education and policy-makers have emphasized the need to advance science education and technology to face the challenges of the globalization era [1,2]. All aspects in education are prepared to make the best strategy in addressing the challenges of the 21st century. One strategy that can be applied is to be actively involved in the science issues. One of the related issues is the enormous challenge of environmental protection caused using chemicals in various fields [3–5]. In addition, chemistry is often regarded as something that is harmful, especially to the environment. An idea was introduced to address this problem called Green Chemistry.

The concept of Green chemistry was introduced in academic circles in the 1980’s by Anastas and Warner, who set sustainability guidelines with a focus on chemistry [6]. These guidelines relate to the application of chemical processes that produce less waste, use small amounts of chemicals...
(microscopic), to apply energy-saving concepts, or to replace harmful and toxic substances with alternative substances. Green Chemistry is closely related to how to overcome environmental problems. This approach is initiated by 12 principles that are expected to respond to the challenges surrounding pollution, energy crisis, waste and work safety. The contribution of this approach is more directed to processes and chemical products that are safer and environmentally friendly also not dangerous for health. Implementation of green chemistry has been done in many fields [7, 8], but few in the field of education. Therefore, researchers want to introduce the idea of Green chemistry by applying chemistry learning based on green chemistry, especially in acid base content. The content was chosen because it has wide application in daily life, especially related to chemical compounds in the household and its relation with chemical industry and the environment of the house [9] and become more interesting to be researched. Learning activities can be applied by doing experiment to identify the nature of acid-base solution using an indicator.

Indicators that are usually used are commercial indicators derived from the synthesis of chemical industries such as phenolphthalein, methyl orange, bromo thymol blue and many others [10, 11]. Commercial indicators have some weaknesses that are expensive and have toxic effects also cause environmental pollution [12]. For this reason, more interest in finding alternative sources of indicators comes from natural resource [13–16]. These alternative indicators will be cheaper, more available, easier to extract, less toxic to users and environmentally friendly. Therefore, the idea to make acid-base indicator derived from natural resource developed by researchers using roses (Rosa's sp) and Rosella (Hibiscus sabdariffa L). The selection of these flowers is because easy to find around the house and traditional markets' also affordable price. The rose and Rosella are renewable material by one of the principles of green chemistry through the use of renewable raw materials to maintain environmental sustainability. Roses and Rosella have anthocyanin substances that act as dye-formers, so they can be used as indicators [17, 18]. The anthocyanin is stable and gives a bright color to acidic pH and will gradually lose color as the pH rises, becoming non-colored at a pH ranging from 4 to 5. The stability of the color of the anthocyanin compound is affected by the pH or acidity level, and will be more stable in acidic atmosphere [19–21].

2. Method
This research was conducted by using roses (Rosa sp.) and Rosella (Hibiscus sabdariffa L) as raw material for making natural acid base indicator. The roses used in this study were obtained in traditional markets in the Tangerang area. The making of this natural indicator is done by extraction method. Fresh roses dried in a way in the wind-air is not dried directly under the sun [18]. Dried roses and Rosella then processed into powder form. After that, the mass of powder roses weighed 20 grams and 10 grams of Rosella for the process of maceration.

The rose and Rosella samples were immersed in 125 mL and 50 mL of 96% ethanol. Firstly, the ethanol was conditioned in acidic conditions (pH 3–4) with the addition of 0.1 M HNO₃ solution. The samples were immersed for 24 hours then filtered using filter paper. The maceration process is repeated three times. The maceration extract is then evaporated until the volume reaches 40-50% of the initial volume. Then, the results of maceration extracted by using n-hexane as much as three times using separating funnel then continued with extraction using chloroform. The final extraction result obtained is used as a natural indicator in the form of solution. After the indicator of roses obtained then tested by using a solution of pH 1-12 to be seen the color changes that occur. The results of the color change that occurs can be used as a color change guide that can be used in learning to identify the nature of acids and bases of a solution. The procedure of making natural indicator of rose extract can be seen in Figure 1.
Figure 1. The procedure of making natural indicator of rose and Rosella extract.

3. Result

The results of solvent extraction from the two samples used showed that the rose extract in the ethanol fraction showed a brownish color while the Roselle extract showed purplish color. The test results of a solution with pH 1 using the rose indicator show purplish pink and gradually fade when the pH rises to 7, then begins to show very faded colors at pH 8 to be blue to green with a pH range of 9-12. These results prove that in red roses, there is anthocyanin dyes that are acidic and red. In alkaline conditions, it will be brown to yellowish green. The anthocyanin stability is strongly influenced by pH so that roses can be used as an alternative raw material as a substitute for commercial acid base indicators [22, 23]. The difference in color seen in a solution with a pH range of 1-12 after adding the rose indicator can be seen in the figure 2.

Figure 2. Change of the color indicators of rose extract to pH solution 1-12.

Similar results were also shown in the test with the Rosella indicator. Testing on a pH 1 solution shows the red color in the solution to pH 3 and then begins to fade at pH 4 to pink and fades to pH 7. Color changes begin to appear at pH 8 that is greenish brown, and more concentrated at pH 8. Testing in a pH 10 solutions show a significant color change at pH 10 to become brownish and changes back to green at pH 11-12. These results show that at increasing pH, the color stability decreases. This can be caused because the structure of anthocyanins is easily changed due to changes in pH [23]. Color differences in solutions with a pH range of 1-12 after the addition of the Rosella flower indicator can be seen in the figure 3.

Figure 3. Change of the color indicators of Rosella extracts to pH solution 1-12.

Furthermore, to apply the indicators in chemistry learning, a simple chemical experiment was performed to determine the acid and base properties of a solution based on Green Chemistry. Before the experiment begins, the researchers provide a simple questionnaire to find out the initial knowledge of students related to green chemistry and whether during this learning at school has applied the principle of green
chemistry. Surprisingly, the results of the questionnaire showed that 30 out of 36 students had no knowledge of green chemistry. They had never applied green chemistry principles in learning whereas it should be applied to involve students actively respond to science issues related to sustainable development [24, 25]. Based on these results, researchers then explain in advance about the principle of green chemistry. The introduction of green chemistry in learning is also supported by performing simple experiments to identify the acid-base properties of some solutions using the extracted rose indicator. Tests were performed using HCl, NaOH, CH₃COOH, and NH₄OH solutions at concentration 0.1 M. This solution was chosen because it's easy to find in the school laboratory so students can do this experiments easily. The results of the experiments obtained can be seen in table 1.

Table 1. Results of identification acid base solution with rose's indicator.

| Solutions | Color Changes       |
|-----------|---------------------|
| HCl       | Faded red           |
| NaOH      | Brownish Green      |
| CH₃COOH   | Pink                |
| NH₄OH     | Yellowish green (faded) |

The process of extraction is a process to obtain the desired substance. Extraction begun with the maceration process followed by solvent extraction using separating funnel. The powdered roses and Rosella were then weighed. The smoothing process was done to increase the surface area of the sample particles so that the anthocyanin dyestuff contained in them is increasingly dissolved in the solvent [26]. The size of the particles of the extracted material is smaller, and the structure of the simpler molecules causes the porosity or the pores of the material to be greater. This situation causes the solvent to diffuse more easily into the cells of the extracted material so that more solutes are dissolved in the solvent. The maceration process of roses and Rosella used as natural acid base indicator was done by using 96% ethanol solvent at room temperature and in the light-absorbent room because anthocyanin stability was affected by temperature, too high a temperature would cause damage to anthocyanin substances [27]. The use of ethanol as a solvent in the maceration process because the polarity of the anthocyanin compound contained in. roses is similar to the polarity of the ethanol solvent so it will be more efficient to get the extract.

At the beginning of the extraction process, it begins with maceration using ethanol, which is conditioned in an acidic atmosphere, because anthocyanin compounds in roses are stable under acidic conditions. After extracting from ethanol, then evaporation using a rotary evaporator is obtained until the extract volume is obtained from 40-50% of the initial volume. After that, it was extracted with n-hexane using a separating funnel to remove residual non-polar substances. Extraction was continued by using a chloroform solvent to remove semipolar residual substances. The results of maceration are extracted again with n-hexane and chloroform solvents to separate other non-polar and semi-polar residues so that the possibility of obtaining anthocyanin extracts in color formation can be greater [28].

Based on the results of experiments conducted by students obtained different color results in four solutions tested using rose extract indicator. Tests on HCl solutions show a faded red color, indicating that the HCl solution is acidic because the anthocyanin pigment in roses will show redness when at low pH [29,30]. The color stability of anthocyanins in roses is strongly affected by the change in pH so that in CH₃COOH solution the color is getting faded but still in the acidic atmosphere. In the solution, NH₄OH obtained a color that faded and showed a yellowish-green color but very faded. This indicates that the pH is increasing, and the solution is base. In NaOH solution, obtained brownish green color, when adjusted to the results of previous indicators test at pH 1-13 can be seen that the green color indicates that the solution has a pH above 10 [30]. During the learning, students look enthusiastic and start thinking related to other alternative materials that can be used as an acid-base indicator. This student response is expected from the application of chemistry-based learning where students are trained to be able to think critically and find solutions-related issues that are being discussed in science. The
application of green chemistry in learning is also expected to improve students' understanding of chemical concepts the ability to think creatively [31] to engage in sustainable development efforts. At the end, acid-base experiment using rose indicator can be said that already apply the principle of green chemistry such as prevention of the formation of hazardous waste, the design of safe chemical products, the use of renewable materials, the design of materials that are easily degraded, and minimize the potential for accidents [32].

4. Conclusion
Based on these results, it can be concluded that the roses and Rosella can be used as an alternative raw material for acid base indicator. The use of roses and Rosella indicates an attempt to apply the concept of green chemistry in chemistry learning. Indicators of roses and Rosella can be said to have applied the principles of green chemistry, including the prevention of the formation of hazardous wastes, the design of safe chemical products, the use of renewable materials, the design of materials that are easily degraded, and the use of safe solvents. It hoped that by applying the concept of green chemistry in learning, students can be more active to engage in science issues and contribute to sustainable development.

References
[1] Kaptan K and Timurlenk O 2012 Challenges for Science Education Procedia - Soc. Behav. Sci. 51 763–71
[2] Anon 2011 This PDF is available from The National Academies Press at
http://www.nap.edu/catalog.php?record_id=13165 A Framework for K-12 Science Education : Practices , Crosscutting Concepts , and Core Ideas A Framework for K-12 Science Education : Practices , Cros
[3] Hartings M R and Fahy D 2011 Communicating chemistry for public engagement Nat. Publ. Gr. 3 674–7
[4] Khalil N, Husin H N, Mahat N and Nasir N 2011 Procedia Engineering Sustainable Environment : Issues and Solutions from the Perspective of Facility Managers 00
[5] Norgate T E, Jahanshahi S and Rankin W J 2007 Assessing the environmental impact of metal production processes 15 838–48
[6] Anastas P T 1999 Green Chemistry and the role of analytical methodology development Crit. Rev. Anal. Chem. 29 167–75
[7] Giraud R J, Williams P A, Sehgal A, Ponnusamy E, Phillips A K and Manley J B 2014 Implementing Green Chemistry in Chemical Manufacturing: A Survey Report
[8] Wardencki W, Curylo J and Namiesnik J 2005 Green chemistry-current and future issues Polish J. Environ. Stud. 14 389–95
[9] Cigdemoglu C, Arslan H O and Cam A 2017 Research and Practice teachers' knowledge, competency, and attitude Chem. Educ. Res. Pract.
[10] Barbosa J 2005 Indicators: Acid–Base Encycl. Anal. Sci. (Second Ed. 360–71
[11] R W S 2007 Handbook of Acid-Base Indicators (San Fransisco: CRC Press)
[12] Saati E A 2015 Anthocyanin Pigment Identification of Batu Local Rose Flower as A Natural Colorant to Replace Harmful Rhodamin B Colorant 6 327–9
[13] Singh S, Bothara S B and Singh S 2011 Acid-Base Indicator Properties of Dyes from Local Flowers : Cassia angustistolia Linn ,, Thevetia peruviana ( Pers .) K . Schum and Thevetia thvetiodes ( Kunth ) K . Schum Pharmacogn. J. 3 35–9
[14] Abbas S K 2012 Study of acid-base indicator property of flowers of Ipomoea biloba Int. Curr. Pharm. J. 1 420–2
[15] Onwuachu U I, Aboh U J U A and Iwuhha G 2014 EXTRACTION , CHARACTERIZATION AND WORKABILITY OF SOME LOCAL PLANT DYES AS ACID-BASE INDICATORS IMPACT Int. J. Res. Applied, Nat. Soc. Sci. 2 1–6
[16] Pathade K S, Patil S B, Kondawar M S, Naikwade N S and Magdum C S 2009 Morus Alba Fruit-Herbal alternative to synthetic Acid Base indicators *Int. J. ChemTech Res.* **1** 549–51

[17] Journal E, Chemistry F and Kanpur T 2015 Rose anthocyanins as acid base indicators

[18] Askar K A, Alsawad Z H and Khalaf M N 2015 Evaluation of the pH and thermal stabilities of rosella anthocyanin extracts under solar light *Beni-Suef Univ. J. Basic Appl. Sci.* 1–7

[19] Choi I, Lee J Y, Laeroix M and Han J 2016 Intelligent pH indicator film composed of agar/potato starch and anthocyanin extracts from purple sweet potato *Food Chem.*

[20] Ge Q and Ma X 2013 Composition and antioxidant activity of anthocyanins isolated from Yunnan *Food Sci. Hum. Wellness* 1–7

[21] Puértolas E, Saldaña G, Álvarez I and Raso J 2011 Experimental design approach for the evaluation of anthocyanin content of rosé wines obtained by pulsed electric fields. Influence of temperature and time of maceration **126** 1482–7

[22] Laleh G . 2006 The Effect of Light, Temperature, pH and Species on Stability of Anthocyanin Pigments in Four Berberis Species *Pakistan J. Nutr.* **5** 90–2

[23] Abou-arab A A, Abu-salem F M and Abou-arab E A 2011 Physico-chemical properties of natural pigments (anthocyanin) extracted from Roselle calyces (Hibiscus subdariffa) 7 445–56

[24] Schaltegger K L S, Barber N A, Wilson F, Venkatachalam V, Cleave S M, Garnham J, Wiek A, Xiong A, Brundiers K and Leeuw S Van Der 2014 International Journal of Sustainability in Higher Education Article information:

[25] Karpudewan M, Ismail Z and Roth W-M 2012 Ensuring sustainability of tomorrow through green chemistry integrated with sustainable development concepts (SDCs) *Chem. Educ. Res. Pr.* **13** 120–7

[26] Jafari S M, Mahdavi-Khazaei K and Hemmati-Kakhki A 2016 Microencapsulation of saffron petal anthocyanins with cress seed gum compared with Arabic gum through freeze drying *Carbohydr. Polym.* **140** 20–5

[27] Henrique P, Jesus R, Spacino I and Tauler R 2011 Investigation of the pH effect and UV radiation on kinetic degradation of anthocyanin mixtures extracted from Hibiscus acetosella OH HO OH OH HO OH OH HO **125** 1020–7

[28] Lapornik B, Prošek M and Wondra A G 2005 Comparison of extracts prepared from plant by-products using different solvents and extraction time *J. Food Eng.* **71** 214–22

[29] Wahyuningsih S, Wulandari L, Wartono M W, Munawaroh H and Ramelan A H 2017 The Effect of pH and Color Stability of Anthocyanin on Food Colorant *IOP Conf. Ser. Mater. Sci. Eng.* **193**

[30] Sukemi S, Purwati W, Pradani S D A, Putra B I, Rahmawati N N and Usman U 2018 Acid Base Indicator from Shoot-Leaves Ethanol Extract of Pucuk Merah (Syzygium oleana) *JKPK (Jurnal Kim. dan Pendidik. Kim.* **2** 139

[31] Nuswowati M, Susilaningshih E, Ramlawati and Kadarwati S 2017 Implementation of problem-based learning with green chemistry vision to improve creative thinking skill and students’ creative actions *J. Pendidik. IPA Indonesia.* **6** 221–8

[32] Anastas P and Eghbali N 2010 Green chemistry: Principles and practice *Chem. Soc. Rev.* **39** 301–12