JKPK (JURNAL KIMIA DAN PENDIDIKAN KIMIA), Vol. 6, No. 3, 2021 pp. 362-370
Chemistry Education Study Program, Universitas Sebelas Maret ISSN 2503-4146
https://jurnal.uns.ac.id/jkpk ISSN 2503-4154 (online)

PREPARATION AND CHARACTERIZATION OF ADSORBENT FROM NATURAL ZEOLITE MIXED CHICKEN FEATHER IN DEGRADATION OF BATIK WASTE DYES BASED GREEN CHEMISTRY

Rais Nur Latifah

Chemistry Department, Faculty of Saint and Technology, Universitas Islam Negeri Walisongo
Jl. Walisongo No.3-5, Tambakaji, Ngaliyan, Semarang, Central Java, 50185, Indonesia

*corespondance email: rais.nurlatifah@walisongo.ac.id

Received: September 28, 2021 Accepted: December 21, 2021 Online Published: December 31, 2021
DOI : 10.20961/jkpk.v6i3.55420

ABSTRACT

This research is the adsorption of dyestuffs from batik industry waste. The adsorption method was used chicken feather adsorbent with natural zeolite. Zeolite was activated by HF. Feather flour was activated with 0.2 M KOH. The main focus of this research is determine the potential for dye degradation with the batch method.Samples were analyzed by Atomic Absorption Spectroscopy (AAS), Fourier Transform Infra Red Spectrophotometer (FTIR), and Surface Area Analyzer (SAA). Measurement of dye degradationincludes the effect of adsorbent concentration, pH, contact time and particle size of adsorbent. The resultsshowed that the optimum pH in the degradation of dyestuffs from the batik industry waste was pH 8.5. Theoptimum contact times by activated and unactivated adsorbents were 65 minutes and 120 minutes, respectively. The reaction kinetics analysis showed the Freundlich adsorption model based on the experimental data. This indicates that the surface pores of the adsorbent are very influential in the degradation of the dye. Adsorption capacity of degradation dyestuffs with adsorbents has an efficiency of 94%. In the laboratory, it has been proven that adsorbents are able to degrade dyes in batik waste before being discharged into thewater disposal system.

Keyword: *chicken feather waste, natural zeolite, adsorbent, batik waste*

INTRODUCTION

Batik is one of Indonesia's cultural heritage. The progress of the batik industry is directly proportional with the batik waste. Pollution is caused batik wastewater. This is main element in environmental pollution [1]. The environmental impact is colored waste and the death of marine life [2]. Pekalongan is one of the centers of the batik industry in Indonesia. There are batik artisans ranging from home industries to large scale. One of the batik home industries produces liquid waste of around 98 L/kg of batik. The main source of this pollution is the dye produced from the rest of the dye, the washing and rinsing process at the end of the batik making process [3]. In addition, batik waste produced is came from wax, residual water in the coloring process and mori residue that used in the batik process [4].

Colors in batik usually used synthetic dyes containing chemical substances.

Examples of batik dyes commonly are used napthol, indigosol and ondanthrene [5]. The process of making batik used large amounts of water and produces a high amount of dye waste. This is directly proportional to the chemical content in the waste which is quite high if the waste treatment is not carried out first before being discharged into water bodies [6].

The dye waste in batik contains 10-15% of the dye that has been used and must be disposed because it cannot be recycled [7]. The dye component in batik waste is a combination of saturated organic molecules with chromophore groups as dyes and auxochromes as color binders with batik cloth fibers [8]. Unsaturated organic components in the process of forming dyes are a group of aromatic compounds, phenols and their derivatives. In addition, there are hydrocarbon compounds containing nitrogen [9]. While the chromophore group is a group of compounds that provide dye in the component.

Many studies have been carried out to overcome batik waste, including ozonation [20], electrochemical coagulation [21] and microbial degradation [22]. The disadvantage of this method is that requires complicated and expensive equipment and methods for the home industry scale. One of the waste treatment methods, cheap and environmentally friendly is adsorption [23]. The adsorption process applies the principle of adsorbent and adsorbate that occurs in a solution with a certain composition and ratio of the adsorbate used. In this study, chicken feather-based adsorbants and zeolite. Chicken feathers is used as adsorbent in processing textile waste due to the content of keratin [24]. Keratin contains N-H groups, C=O, O-H, COOH and S-H. The keratin content of chicken feathers is 85- 90%. Protein content in chicken feathers is 60-80%. Keratin or fiber consists of cystine disulfide bonds, hydrogen bonds, and interactions hydrophobicity of protein molecules [10]. Zeolite is an adsorbent that has pores that can absorb molecules that have a smaller diameter [11]. Besides, zeolite has a cation exchange capacity with high selectivity [12]. This study aims to degrade the dye in batik waste.

METHODS

1. Materials

Zeolite preparation and activation used H_3PO_4 and HF from Sigma–Aldrich (Steinheim, Germany). Textile Synthetic Waste used indigosol. Chicken feathers are obtained from chicken waste at Nusukan Market, Central Java. Activation of chicken feathers used KOH from Sigma–Aldrich (Steinheim, Germany). Aquades is used as a solvent.

2. Preparation of Textile Synthetic Waste

Synthetic waste was prepared with various concentrations of 10, 30, 50, 70, and 100 ppm.

3. Preparation of natural zeolite as adsorbent

Natural zeolite is taken from Klaten, Central Java as one of the largest zeolite producers. Natural zeolite was pulverized and sieved with a size of 100 mesh. Then the zeolite was washed with distilled water and dried in an oven at 100°C for 2 hours. 10 grams of zeolite was immersed in 100 mL of

3.5 M H_3PO_4 solution for 24 hours with a shaker and stirrer. Then it was washed again with distilled water and dried in an oven for 3 hours at 60°C.

4. Preparation of Chicken Feathers as Adsorbent

Chicken feathers were taken from a chicken farm in Wonorejo Village, Karanganyar, Central Java. Feather chicken is a type of free-range chicken. Then the chicken feathers are cleaned of dirt and washed with water until clean until thesmell and dirt disappear. Chicken feathers are cut into small pieces and ground toa size of 150 mesh. The chicken feathers were washed again with distilled water then with alcohol for 60 minutes and dried with freeze dry.

5. Chicken Feather Activation

10 grams of chicken feather flour was taken and activated with 0.2 M KOH as much as 50 mL then stirred with a shaker and stirrer for 60 minutes. The solution was filtered to use a Buchner funnel and dried in an oven at 60°C. The activated chicken feathers were characterized by FTIR.

6. Activation of Natural Zeolite

Zeolite activation process: 30 grams of zeolite mixed with 180 mL of 1.5% HF. Then the stirring process was 12 hours at a temperature of 25°C. Then the washing process with distilled water 3 times and drying in an oven at a temperature of 60°C.

7. Adsorption-Desorption of Textile Waste Dyes with Natural Zeolite Mixed Chicken Feather

Textile waste solution was put into 5 Erlenmeyer 25 mL as much as 10 mL. The adsorbent pellet was put into an Erlenmeyer. Then the solution was stirred for 90 minutes with a stirring speed of 25 rpm. The solution was filtered, the filtrate was obtained by using AAS. Then the adsorbent was put back into the second beaker and stirred for 90 minutes and the content of the textile waste dye was not adsorbed again. The treatment was repeated for the second to fifth glasses.

8. Data Analysis

The concentration of adsorbed waste for each treatment was calculated from:

$$Ca = Co - Ct \qquad (1)$$

The amount of adsorbed waste (mg) per gram of adsorbent is determined the equation:

$$qe = \frac{(C_0 - C_t)V}{W} \qquad (2)$$

Description:

qe : adsorbed waste rate (mg/g)

C_0 : initial concentration (mg/L)

C_t : final concentration (mg/L)

V : solution volume (L)

W : weight of adsorbent (g)

The adsorption capacity is calculated from the Langmuir equation (Ce/qe = 1/Qob + Ce/Qo) or Freundlich's equation [log(x/m) = log k + 1/n (log C) with plot Ce/qe against Ce for the Langmuir equation or the equation Freundlich obtained the value of k (adsorption capacity) and from the slope of the equation Langmuir can obtain the value of Qo which is related to the adsorption capacity.

RESULTS AND DISCUSSION

1. Adsorbent

Adsorbent is a combination of natural zeolite and chicken feather flour, each of absorbent has been activated. The activation process used an alkaline solution and H_3PO_4 at a certain temperature to create a space between the pores so that the adsorbed substance can penetrate the small pores and stick to the adsorbent. The results of the analysis with the Survace Area Analyzer (SAA) instrument resulted in surface area data presented in Table 1.

Table 1. Result of surface area analysis.

Adsorbent	Surface area (m^2/g)
Natural zeolite	42.17
Activated natural zeolite	78.56
Chicken feathers	54.13
Activated chicken feathers	96.82

Based on Table 1, it shows activated natural zeolite with a higher surface area than without activation. Activated natural zeolite experienced an increase in surface area of 46.32%. Meanwhile, after the activation process, activated chicken feathers have a higher surface area than unactivated feathers. It is used to adsorb chemical components in batik waste in the adsorption process.

Table 2. Pure volume data from chicken feathers

Method	Pore volume data
HK method cumulative pore volume	3.625e-02 cc/g
SF method cumulative pore volume	3.974e-02 cc/g

The activation process in chicken feathers aims to break the disulfide bond bridge (-S-S-). The results of the FTIR analysis showed that the absorption region of the peptide bond (-CONH-), the vibration in that area was the absorption region of amide I-III.

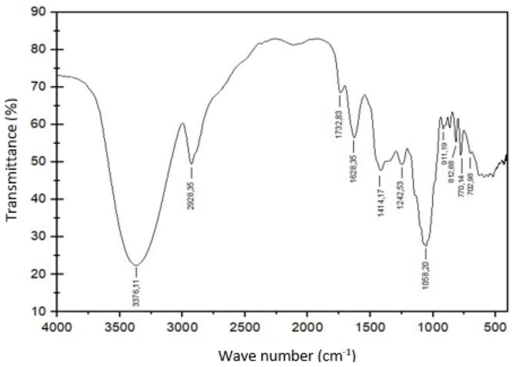

Figure 1. Spectra FTIR of chicken feathers

Besides chicken feathers, adsorbents are made from natural zeolite. The zeolite activation process used the acid method that through an ion exchange mechanism between metal cations from zeolite and H+ from acid [13].

Table 3. FTIR results of chicken feathers

ƛ (cm^{-1})	Functional Groups
1628	Amida I = vibrasi stretching C=O
1414	Amida II = vibrasi bending N-H danstretching C-H
1242	Amida III = vibrasi stretching C-N dan bending sebidang N-H

Zeolite pore volume has increased to 3.625e-02 cc/g. Zeolite activation causes the zeolite surface to be larger than its original size [14]. The activation process causes damage to the zeolite framework structures, O-Si-O and O-Al-O are replaced with silanol (≡SiOH) and aluminol (=AlOH) groups [15].

Some of the hydroxide groups (-OH) are replaced by -OH + [14]. The replacement of this group increases the surface area and pore diameter of the zeolite. The following at Figure 2 is the activation reaction of the zeolite.

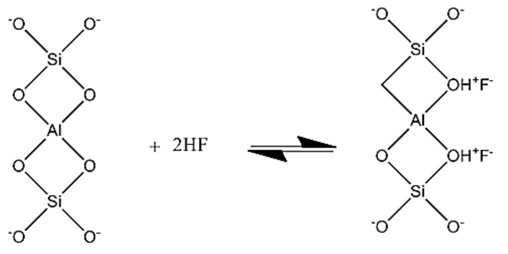

Figure 2. Natural zeolite activation reaction with HF.

The zeolite is used an activation process. It aims to open the pores of the zeolite [16]. 20-50% of the total volume of the open zeolite pores through the activation of the aluminosilicate structural framework and the intercrystalline cavity of the zeolite [14]. The activated zeolite can trap the adsorbate by the process of dehydration and hydrogen bonding that occurs between the adsorbent and the adsorbate [17].

2. pH Analysis on Textile Waste Dyestuff Degradation

pH is one of the factors that affect the adsorption process. pH played a role in the analysis of functional groups in the wall mass of chicken feather biomass. Optimum pH was determined from the absorbent work in degradation waste.

Batik waste is used a synthetic waste solution with a concentration of 60 ppm with a contact time of 90 minutes. Each adsorbent has optimum conditions at pH 8.5 with an adsorbed efficiency at 98.25% and 73.21%, for activated and inactivated adsorbents. The pH of the textile waste solution affects the work of the adsorbent in adsorption of textile waste, which is optimum under alkaline conditions.

Table 4. The results of the analysis pH from adsorbent with the efficiency of the absorbed batik waste.

pH	Adsorbed Efficiency	
	Activated	Not activated
3.5	39.37	26.71
4.5	56.49	42.57
5.5	62.55	49.21
6.5	67.89	54.25
7.5	72.67	60.59
8.5	98.25	73.21
9.5	83.26	59.56
10.5	79.11	58.23

One of the dyestuffs in textiles is indigosol. This type of dye is obtained dye with a fixed composition, it had many color choices and easy to apply at a low price. The following is the structure of indigosol [12].

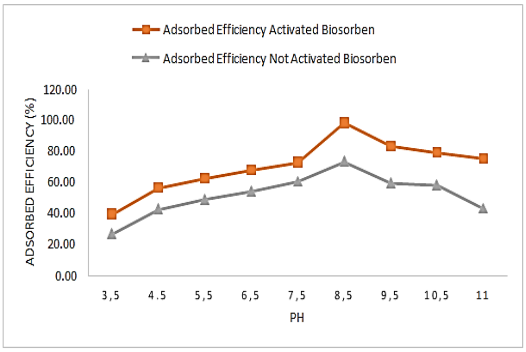

Figure 3. Efficiency if adsorbed waste.

Indigosol was the potential pollute environment [18]. At pH above 3, indigosol was released H+ which interacts with the thiol group of the adsorbent (-SH) [19]. This caused an increase strong interaction between the two specimens. Meanwhile, at pH above 8, the dye waste was begun

NaO3SO- structure which caused the ionization of the cysteine side chain, namely the thiol group (-SH). That was caused attraction of NaO3SO- to the adsorbent.

3. Effect of Concentration on Degradation of Textile Waste Dyes

Concentration was a parameter in determining the optimum conditions for batik waste. The concentration of adsorbed waste is related the number of active sites on the surface of the adsorbent, if the number of active sites on the adsorbent is greater than the amount of adsorbate to be absorbed, the absorption efficiency will be constant because there has been saturation of the adsorbent. Higher concentration of the adsorption process was caused higher efficiency of adsorption by the adsorbent. Based on the adsorption process, the optimum concentration was 52.48 ppm with an adsorbed efficiency at 94.32%. Meanwhile, the unactivated adsorbent had an adsorbed efficiency of 72.13% at 63.21 ppm.

At a concentration of 52.48 ppm adsorbent, the adsorbent performs had many physical interactions with textile waste. There was a collision between atoms in the adsorbent with the waste on the surface adsorbent active site. The dye waste is adsorbed in the pores zeolite surface. This was undergoes a physical process in the adsorption process, followed by a chemical reaction with chicken feathers on the thiol group of the adsorbent. At concentrations above 60 ppm, the efficiency of adsorption tends constant. This was indicated a balance point between the adsorbent and its environment.

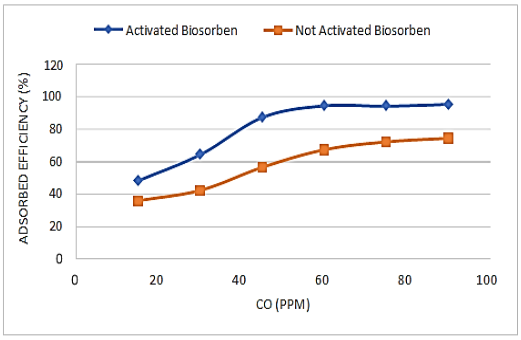

Figure 4. Efficiency of adsorbed dye degradation with adsorbent concentration.

This adsorbent concentration was determined with reaction mechanism in absorbing dyes in textile waste. Zeolite which has an active site from adsorbent will absorb H+ from waste. The H+ is strongly attracted oxygen atoms. That is followed van der Walls bonds. The dye has been adsorbed adsorbent then it through chemical adsorption with the active site of the chicken feather. The amide group in chicken feathers was degradeyed the dye chemically to purify textile waste. Furthermore, adsorption and desorption processes were occured in textile waste through chemical exchange of cation and anion groups. The possible mechanisms were occured in the adsorption process in Figure 4. This was happened at the beginning of the absorption, the surface of the adsorbent is still not very good to bind with the waste so that the absorption process takes place less effectively. The surface adsorption capacity of the biomass has been saturated and an equilibrium between the adsorbate concentration in the biomass and the environment, so that optimal absorption was occured at concentrations above 80 ppm.

4. Optimum Contact Time

Contact time is one of the parameters in the adsorbent adsorption method on the degradation of textile waste dyes. Contact time is done after determining the optimum pH. The results of the time test are shown in the Figure 5 below.

Based on the graph, the degradation of dyes had optimum absorption at 65 and 120 minutes, for activated and inactivated adsorbents. The adsorbents were interacted a lot of batik dye waste which is adsorbed on the surface of the adsorbent. After the optimum absorption at that minute, the dye absorption was tend constant at a time duration more than 100 minutes. The factor influences was the adsorbent that has reached the saturation point of the absorption of the waste. In addition, this was an equilibrium point that has been reached between the adsorbent and environmental conditions. This is called the adsorption equilibrium. When the optimum condition of the adsorbent was the dye degradation absorption process. That had maximum absorption capacity value. Then after the equilibrium point, the adsorbent undergoes a desorption process.

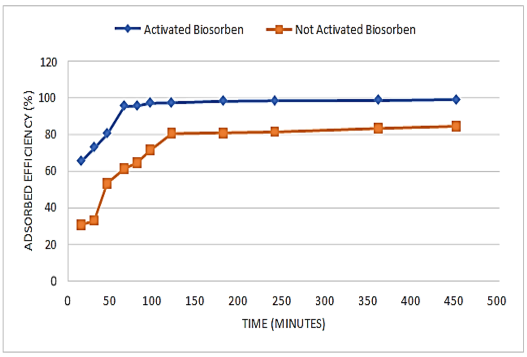

Figure 5. Optimum contact time for dye degradation.

5. Study of Adsorption Isotherms

The study of adsorption isotherms was investigated for activated adsorbents. The adsorption process for dye degradation of batik waste used adsorbent tends to follow the Freundlich isotherm.

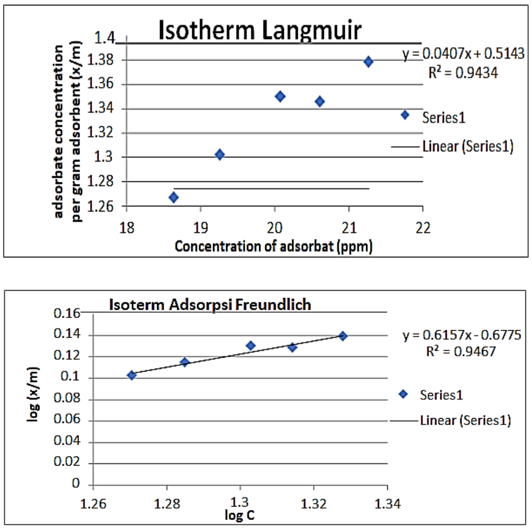

Figure 6. Adsorption isotherms curves (a) Langmuir, and (b) Freundlich

The adsorption process was influenced dominantly by the pores of the adsorbent compared to the exchange of active groups between the adsorbent and the adsorbate. The zeolite pores had a larger size which absorb the dye in the batik waste. Then an adsorption process will be carried out on the chicken feather biomass. Chicken feathers will degrade the chemical content in batik waste then the adsorbate will be adsorbed.

CONCLUSION

The adsorbent degrades the dye with an optimum condition at 60 ppm, contact time of 90 minutes and pH of 8.5. The adsorption process for dye degradation of batik waste used adsorbent follows the Freundlich isotherm. The use of adsorbents made from chicken feather waste that one of the efforts to achieve environmental cleanliness based on green chemistry. In addition, green chemistry in this research is shown by eliminating waste and formation of toxic and dangerous chemicals after the dye adsorption process in waste.

ACKNOWLEDGEMENT

Appreciation to UIN Walisongo Semarang for research and publication assistance.

REFERENCES

[1] V. N. June and J. Cover, "Improvement of Batik Liquid Waste Quality with IPAL Mini Technology: Case on Flower Tourism Sidomulyo Village in Batu, Indonesia," *Bus. Econ.*, vol. 1, no. 1, pp. 1–13, 2019, DOI: 10.21070/ijccd2021690.

[2] S. Budiyanto, Anies, H. Purnaweni, and H. R. Sunoko, "Environmental Analysis of the Impacts of Batik Waste Water Polution on the Quality of Dug Well Water in the Batik Industrial Center of Jenggot Pekalongan City," *E3S Web Conf.*, vol. 31, no. 2, 2018, DOI: 10.1051/e3sconf/20183109008.

[3] I. Fajriati, Mudasir, and E. T. Wahyuni, "Adsorption and photodegradation of cationic and anionic dyes by TiO 2 - chitosan nanocomposite," *Indones. J. Chem.*, vol. 19, no. 2, pp. 441–453, 2019, DOI: 10.22146/ijc.38278.

[4] P. Susmanto, Y. Yandriani, A. P. Dila, and D. R. Pratiwi, "Pengolahan Zat Warna Direk Limbah Cair Industri Jumputan Menggunakan Karbon Aktif Limbah Tempurung Kelapa pada Kolom Adsorpsi," *JRST (Jurnal Ris. Sains dan Teknol.*, vol. 4, no. 2, p. 77, 2020, DOI: 10.30595/jrst.v4i2.7309.

[5] V. No, L. A. Yoshi, J. A. Idat, and G. Maulidyananda, "Upaya Penurunan Nilai COD pada Limbah Tekstil dan Batik dengan Penambahan NaOCl," *Al-Ard J. Tek. Lingkung.*, vol. 6, no. 1, pp. 37–43, 2020, DOI: 10.29080/alard.v6i1.954.

[6] Y. L. Ni'Mah, I. Rohmawati, I. Ulfin, Harmami, H. Junowo, D. Sugiarso, F. Kurniawan, and Suprapto, "The adsorption of remasol, indigosol and naphtol yellow mixed dyes using activated carbon," *AIP Conf. Proc.*, vol. 2229, no. April, 2020, DOI: 10.1063/5.0002666.

[7] A. Qisti, Y. Utomo, and D. A. Rokhim, "Treatment of Dye Wastewater from Batik Industry by Coconut Shell Activated Carbon Adsorption," *Fuller. J. Chem.*, vol. 6, no. 1, p. 7, 2021, DOI: 10.37033/fjc.v6i1.213.

[8] N. Sharfan, A. Shobri, F. A. Anindria, R. Mauricio, M. A. B. Tafsili, and Slamet, "Treatment of batik industry waste with a combination of electrocoagulation and photocatalysis," *Int. J. Technol.*, vol. 9, no. 5, pp. 936–943, 2018, DOI: 10.14716/ijtech.v9i5.618.

[9] N. K. T. Martuti, I. Hidayah, M. Margunani, and R. B. Alafima, "Organic material for clean production in the batik industry: A case study of natural batik Semarang, Indonesia," *Recycling*, vol. 5, no. 4, pp. 1–13, 2020, DOI: 10.3390/recycling5040028.

[10] P.-R. Me and H.-M. Dj, "Degradation of Chicken Feathers : A Review," *Biotechnol. An Indian J. Rev.* |, vol. 13, no. 6, pp. 1–24, 2017, [Online]

[11] G. Budiyanto, "The Application of Zeolite to Increase Nitrogen Use Efficiency in Corn Vegetative Growth in Coastal Sandy Soils," *Planta Trop. J. Agro Sci.*, vol. 8, no. 1, pp. 1–6, 2020, DOI: 10.18196/pt.2020.107.1-6.

[12] R. S. Dewi, R. S. Kasiamdari, E. Martani, and Y. A. Purwestri, "Decolorization and detoxification of batik dye effluent containing Indigosol Blue-04B using fungi isolated from

contaminated dye effluent," *Indones. J. Biotechnol.*, vol. 23, no. 2, pp. 54–60, 2018,
DOI: 10.22146/ijbiotech.32332.

[13] S. Amelia and M. Maryudi, "Application of Natural Zeolite in Methylene Blue Wastewater Treatment Process by Adsorption Method," *J. Bahan Alam Terbarukan*, vol. 8, no. 2, pp. 144–147, 2019,
DOI: 10.15294/jbat.v8i2.22480.

[14] B. Pich, I. W. Warmada, H. Hendrayana, and T. Yoneda, "Modified Natural Zeolite and Bentonite As Adsorbents of Heavy Metal Ions From Polluted Groundwater in Yogyakarta Urban Are, Indonesia," *J. Appl. Geol.*, vol. 2, no. 1, pp. 91–97, 2015,
DOI: 10.22146/jag.7229.

[15] E. Heraldy, H. SW, and S. Sulistiyono, "Characterization and Activation of Natural Zeolit From Ponorogo," *Indones. J. Chem.*, vol. 3, no. 2, pp. 91–97, 2010,
DOI: 10.22146/ijc.21891.

[16] O. Nurwidanti and N. Hidayat, "Teknologi Dekolorisasi Limbah Cair Batik dengan Menggunakan Zeolit dan Arang Termodifikasi Pada Sistem Kontinyu," *J-Pal*, vol. 7, no. 2, pp. 96–103, 2016,
DOI: 10.1051/e3sconf/20183109008.

[17] S. Maharani, L. Nailufhar, and Y. Sugiarti, "Adsorption effectivity of combined adsorbent zeolite, activated charcoal, and sand in liquid waste processing of agroindustrial laboratory," *IOP Conf. Ser. Earth Environ. Sci.*, vol. 443, no. 1, 2020, DOI: 10.1088/1755-1315/443/1/012044.

[18] S. N. Chattopadhyay, N. C. Pan, A. K. Roy, and A. Khan, "Dyeing of jute fabric using indigosol dyes," *J. Nat. Fibers*, vol. 6, no. 1, pp. 98–107, 2009, DOI: 10.1080/15440470802703596.

[19] D. gosal, rosalia., "Biodegradasi Zat Warna Indigosol Golden Yellow Irk Menggunakan Biosistem Vertikal," *Ecotrophic*, vol. 12, no. 1, pp. 34–41, 2018.

[20] N. Annisa, M.S. Nadisti, E. F. Karamah, and S. Bismo, "Degradation of Batik Dye Wastewater in Basic Condition by Ozonation Technique in Bubble Column Reactor," *E3S Web of Conferences,* vol.67, 2018. DOI: 10.1051/e3sconf/20186704019

[21] Riyanto, E. Puspitasaril, "Treatment of Wastewater Batik by Electrochemical Coagulation Using Alumunium (Al) electrodes, "*IOP Conf. Series : Mat Sci and Eng,* vol. 299, 2017.
DOI: 10.1088/1757-899X/299/1/012081.

[22] B. Muchtasjar, H. Haiyanto, and M. Izzati, "Microbial Degradation of Batik Waste Water Treatment in Indonesia," *IOP Conf. Series : Earth and Env Sci*, vol. 314, 2019,
DOI: 10.1088/1755-1315/314/1/012020.

[23] P. A. Handayani, U. Cholifah, R. Ulviana, and A. Chafidz, "Batik, Industri Wastewater Treatment via Coagulation-Flocculation Process and Adsorption Using Teak Sawdust Based Activated Carbon", *Jurnal Bahan Alam Terbarukan,* vol. 8, no. 1, pp: 8-13, 2019,
DOI 10.15294/jbat.v8i1.20144.

[24] B. Y. Alashwal, A. Gupta, and M. S. B. Husain, "Characterization of Dehydrated Keratin Protein Extracted from Chicken Feather", *IOP Conf. Series : Mat Sci and Eng.* Vol. 702, 2019,
DOI: 10.1088/1757-899X/702/1/012033.