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To cite this article: M. Nurhadi *et al* 2021 *J. Phys.: Conf. Ser.* **1842** 012047

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The Removal of Methylene Blue and Congo Red Dyes from Aqueous Solution by Using Sulfonated Carbon Derived Fishbone

M. Nurhadi¹, R. Kusumawardani¹, M. Rindoi¹, A. D. Apriliani¹, A. F. Khair¹, A. Noor¹, T. P. Lumbantobing¹

¹Department of Chemical Education, Universitas Mulawarman, Kampus Gunung Kelua, Samarinda, 75119, East Kalimantan, Indonesia

Corresponding author's: nurhadi1969@yahoo.co.id

Abstract In the world, the dyes pollutant from industrial activity is big issue that must be sought the solution. Among of dyes pollutants were methylene blue (MB) and congo red (CR). In this research have been conducted the removal of methylene blue and congo red onto sulfonated carbon derived fishbone (SCFB) as adsorbent from aqueous solution. The preparation steps of SCFB adsorbent involved the sulfonation (H_2SO_4 ; 1M) of fishbone powder for 6 h, by stirrer at room temperature, and followed by carbonization at 500 °C for 2 h. The physical properties of the adsorbents were characterized using Fourier Transform Infrared, X-Ray Diffraction (XRD), and nitrogen adsorption-desorption studies. The dye removal study using SCFB adsorbent was carried out by varying contact time and initial dye concentration. The kinetics models were determined by the effects of contact time. The adsorption isotherms were tested to isotherm Langmuir and Freundlich with a base on the effect of initial dye concentration. The result showed that The removal of MB and CR dyes using SCFB adsorbent fitted a pseudo-second-order kinetic models. The maximum dye removal capacity of SCFB was 128.2 mg g⁻¹ for CR and 35.7 mg g⁻¹ for MB. Base on the maximum dye removal capacity, the SCFB can be considered as good adsorbent to remove dyes pollutant from environment.

1. Introduction

Dyes pollutant was a big problem in the world that must be overcome. Many kinds of dyes pollutants have been released from industrial activity such as textile, paint, plastic, rubber, leather, cosmetic [1][2], and drug. Dyes pollutant was the main environmental problem due to not degraded properties, stable under light, and oxidation. Therefore, the removal of dyes pollutants from the environment is urgent.

Many methods have been applied to removal dyes pollutant from wastewater such as photochemical degradation[2], biological degradation [3], chemical oxidation [4], electrocoagulation [5], coagulation and flocculation [6], adsorption [7-10], ozonation[11], fungal decolorization [12]. Among these methods, adsorption is familiar used due to the fast way, easy process, low cost, and also high efficiency [7]. A lot of adsorbents have been tested to remove dyes from wastewater such as zeolite [10], bentonite, montmorillonite, clay [1], chitosan [11], algae [12], cellulose [13], and carbon-derived from *Eichhornia crassipes*[1, 13].

Here, the sulfonated carbon derived fishbone (SCFB) has been used to adsorb methylene blue (MB) and congo red (CR) dyes. The dye removal capacity, the effect of contact time, and the effect initial concentration of dyes have investigated. The Freundlich and Langmuir isotherm was used to check the



adsorption isotherm. The pseudo-first-order and the pseudo-second-order were used to check the kinetics process in the adsorption of the dyes. The maximum dye removal capacity was determined by the Langmuir equation.

2. Materials and Methods

2.1. Carbonization process

The fish bones powder was immersed into a sulfuric acid solution (1 M) under a stirrer at room temperature for 6 h. Then, the sulfonated of the fish bones powder was dried in an oven at 110 °C for 24 hours. The dry of sulfonated fish bones powder was calcined in a furnace at 500 °C for 2 hours. The powder obtained after calcination was labeled as SCFB.

2.2. Samples Characterization

The SCFB sample was characterized by using the Fourier transform infrared spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), and nitrogen adsorption-desorption studies. The FTIR spectroscopy (IR–Prestige–21 Shimadzu) was used to determine the functional groups in the sample. The XRD (Phillips PANalytical X'Pert PRO type), with the Cu K α ($\lambda = 1.5406 \text{ \AA}$) radiation was used to investigate the crystallinity and phase content of the sample. The data collected from a Quantachrome nova 1200e instrument was used to determine the nitrogen adsorption-desorption isotherms, surface area, micropore area, and pore size distribution of the sample.

2.3. Adsorption test

The adsorption test of the sample was done to Methylene blue ($C_{16}H_{18}ClN_3S \cdot xH_2O$, $x = 2-3$; Merck) and Congo red ($C_{32}H_{22}N_6O_6S_2$, Merck) dyes. The adsorption was carried out by mixing 0.250 g the adsorbent with 25 mL of MB solution (100 mg L^{-1}) or 0.0625 g adsorbent with 25 mL of CR dye solution (100 mg L^{-1}) in a 100 mL beaker glass at room temperature for the duration of 5, 10, 15, 20, 25, 30, 60, 120 min. Furthermore, the adsorbent was separated from the filtrate by centrifugation and the residual dye in the filtrate was analyzed by using UV-Vis spectrophotometer by monitoring the changes in absorbance at 660 nm for MB and 550 nm for CR. The effect of initial dye concentration was investigated by varying initial concentrations 100, 200, 300, 400, 500, 600, and 800 mg L^{-1} .

The adsorption capacity q_t of adsorbent (mg/g) was calculated with following the equation[14, 15]:

$$q_t = (C_0 - C_t) \cdot V/W \quad (1)$$

where C_0 is the dye initial concentration and C_t is the dye concentration after adsorption time t (mg L^{-1}) in the solution, V is the volume of dye solution (mL) and W is weight adsorbent (g).

The pseudo-first-order kinetic models and the pseudo-second-order kinetic model were used to test the adsorption kinetic of MB and CR adsorption onto SCFB adsorbent. The pseudo-first-order kinetic models' expression of Lagergren base on the sorption capacity of adsorbent is expressed as[16-18]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

where k_1 (g/mg.h) is the rate constant for Lagergren pseudo-first-order, q_e and q_t are the amounts of dye adsorbed per gram of adsorbent (mg/g) at equilibrium and any time t . The value of k_1 and q_e can be determined from the slope and intercept from plot $\ln(q_e - q_t)$ versus t .

The pseudo-second-order kinetic model is also based on the sorption capacity of the adsorbent. The linear form of the pseudo-second-order kinetic model was expressed by Ho, Y. S., and McKay, G with the equation[19, 20]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where k_2 ($\text{g mg}^{-1} \text{h}^{-1}$) is the rate constant for pseudo-second-order, q_e and q_t are the amounts of dye adsorbed per gram of adsorbent (mg g^{-1}) at equilibrium and any time t . The value of k_2 and $q_{e,\text{cal}}$ can be calculated from intercept and slope from the plot t versus t/q_t .

The Langmuir and the Freundlich isotherm were used to investigating the adsorption isotherm of the adsorption process onto SCFB adsorbent. The Langmuir isotherm is correlated with monolayer sorption onto a surface. The Langmuir equation is given by [21-23]:

$$\frac{C_e}{q_e} = \frac{1}{Q_{max}} C_e + \frac{1}{Q_{max} \cdot b} \quad (4)$$

where Q_{max} and b are Langmuir constant which correlated with maximum adsorption capacity and bonding energy of adsorption, respectively. The slope and intercept of the linear plot of $\frac{C_e}{q_e}$ versus C_e were used to determine Q_{max} and b .

The Freundlich isotherm model assumes heterogeneous site energies of sorption. The Freundlich equation is followed as [14, 22]:

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e \quad (5)$$

where K_F and n are the Freundlich constant which indicates adsorption capacity and adsorption intensity, respectively. The intercept and slope of the plot of $\ln q_e$ versus $\ln C_e$ were used to calculate K_F (mg g^{-1}) and n (L mg^{-1})^{1/n}.

3. Results and discussion

3.1. Physical properties

Figure. 1 shows the infrared spectra of the surface functional groups of SCFB. The samples showed a broad peak at around 3613 and 1619 cm^{-1} were assigned to the $-\text{OH}$ stretching vibration mode of the $-\text{COOH}$ group which correlated adsorbed water in the sample. The peaks at around 2925 and 2851 cm^{-1} were correlated to the absorption of organic material as C-H group symmetric and asymmetric stretching mode which were caused by the carbonization process. The hydroxyapatite in the sample was investigated by carbonate ion and phosphate groups. The absorption peak at around 2129 and 809 cm^{-1} indicates the carbonate ion substitution in the sample. And the peak at around 679 and 612 cm^{-1} correlated with the phosphate groups on the sample. The effect of the sulfonation process was proven by the adsorption band at 1122 and 1013 cm^{-1} which indicated the attachment of $-\text{SO}_3\text{H}$ groups onto the sample. The adsorption band at 1122 cm^{-1} indicated $\text{O}=\text{S}=\text{O}$ symmetric stretching in $-\text{SO}_3\text{H}$ and 1013 cm^{-1} was related SO_3^- stretching mode.

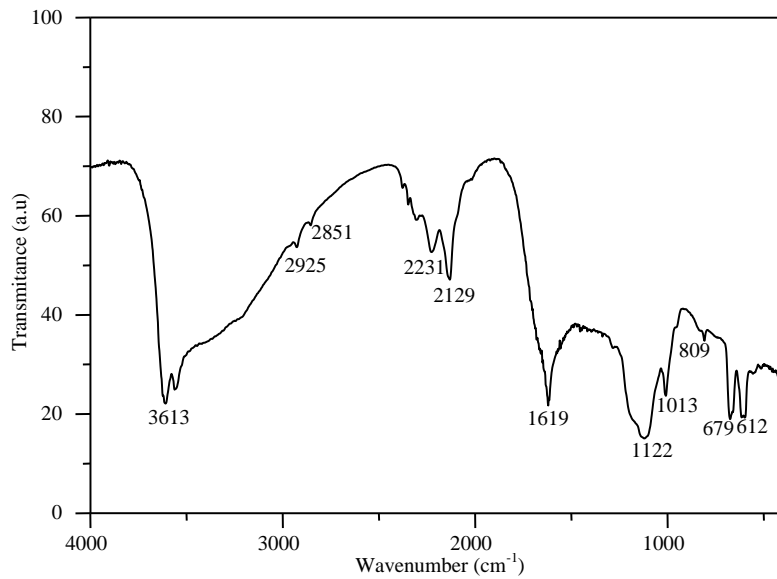


Figure 1. Infrared spectra of SCFB

Figure 2 showed the XRD pattern of SCFB. The peaks at the angles of $2\theta = 25.9, 31.8, 39.8, 46.8, 49.6, 53.4,$ and 64.4 indicated that the sample was dominated by the crystalline phase of hydroxyapatite.

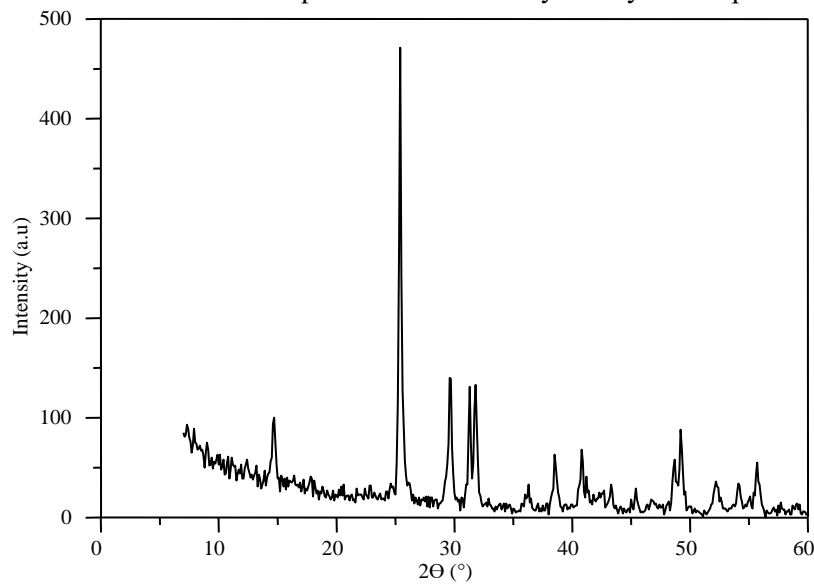


Figure 2. XRD pattern of SCFB

Figure 3 shows the N₂ adsorption-desorption isotherms of SCFB. The Isotherm of the SCFB sample is type IV patterns in the IUPAC classification with clear hysteresis loops in the relatively low-pressure range that indicates the presence of mesopores. The hysteresis loops type of SCFB is type H₁ which is often identified with porous materials exhibiting a narrow distribution of relatively uniform (cylindrical-like) pores. The pore size distribution of the FB sample indicated the presence of uniform pores with a pore radius ~9 nm. The pore radius, pore-volume, and surface area of the SCFB sample were 9.35 nm, 0.0747 cc/g, and 15.97 m²/g, respectively.

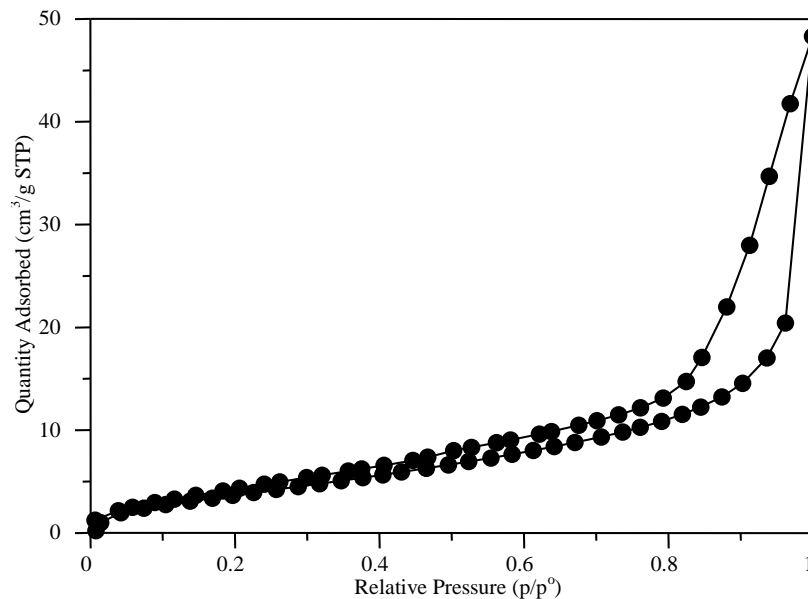


Figure 3. N₂ adsorption-desorption isotherms of SCFB

3.2. Dyes Removal

The removal of congo red and methylene blue onto SCFB adsorbent by the effect of contact time was shown in Figure 4. Both dyes were drastically adsorbed onto SCFB in 5 min duration with the amount dye adsorbed at the removal capacity for MB and CR are 85.89 and 93.79 mg L⁻¹ or 8.59 and 37.52 mg g⁻¹, respectively. The amount dye adsorbed or the removal capacity of both dyes onto SCFB adsorbent increase slightly in duration time 5 to 30 min. And it almost stable in duration time 30 to 120 min. the adsorption process onto SCFB for CR and MB have reached the equilibrium with the removal capacity of 39.76 mg g⁻¹ (CR) and 8.90 mg g⁻¹ (MB). In this research, the removal capacity of Congo red higher than Methylene blue. This result inline with the previous research adsorption congo red and methylene blue onto carbon derived[13].

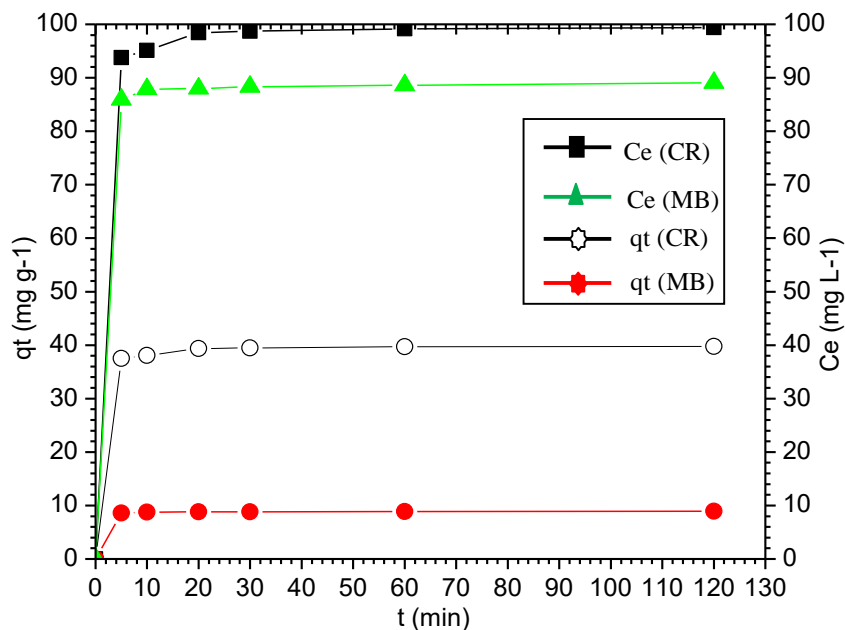


Figure 4. Effect of contact time on congo red and methylene blue dye removal. Conditions: (pH: 6.9, MB: 100 mg.L⁻¹, weight adsorbent: 250 mg, at 30 °C).

3.3. Adsorption of kinetic

The pseudo-first-order and pseudo-second-order kinetic models were used to investigate the kinetics process of MB and CR dyes adsorption experiment onto SCFB adsorbent. Based on the experiment results, the removal of MB and CR onto SCFB adsorbent did not fit a pseudo-first-order reaction model due to the correlation coefficients $R^2 \ll 1.000$ and the dyes removal capacity calculated ($q_{e, cal}$) \ll the removal of the dyeing capacity experimental ($q_{e, exp} = 8.905 \text{ mg g}^{-1}$ for MB; 39.763 mg g^{-1} for CR). Otherwise, the adsorption process of MB and CR dyes showed good compliance with the pseudo-second-order. This was proven by the value of correlation coefficients (R^2) for linear plots for MB and CR removal on to SCFB adsorbent was 1.000. The value of rate constant (k_2) of the removal of the dyes onto SCFB was 0.0012 (CR) and 0.7414 (MB). And the value of the calculated dyes removal capacity ($q_{e, cal} = 8.881 \text{ mg g}^{-1}$ (MB) and 39.840 mg g^{-1} (CR)) of both dyes were close with the value of the experiment dyes removal capacity ($q_{e, exp} = 8.905 \text{ mg g}^{-1}$ (MB) and 39.763 mg g^{-1} (CR)). The complete results are shown in Table 1. This phenomenon is in line with previous researches that have been reported in the reference for different adsorbate dyes [24].

Table 1 First order and Pseudo second-order kinetics for CR and MB dyes adsorption on SCFB adsorbent

Dye removal	Pseudo First Order			Pseudo Second Order			$q_{e, exp}$ (mg g^{-1})
	$q_{e, cal}$ (mg g^{-1})	k_1 ($\text{g mg}^{-1} \text{ h}^{-1}$)	R^2	$q_{e, cal}$ (mg g^{-1})	k_2 ($\text{g mg}^{-1} \text{ h}^{-1}$)	R^2	
CR	2.193	0.0010	0.8951	39.840	0.0012	1.000	39.763
MB	0.2160	0.0282	0.7606	8.881	0.7414	1.000	8.905

3.4. Effect of initial concentration

Figure 5 showed the effect of initial concentration for Congo red and Methylene blue onto SCFB adsorbent. The removal capacity of both dyes onto SCFB adsorbent has a trend increase from 39.8 to 129.9 mg g^{-1} (CR) and 8.9 to 27.4 mg g^{-1} (MB) for initial concentration 100 to 600 mg L^{-1} . The increasing of the removal capacity at equilibrium condition was caused by an increasing the initial concentration that can increase the driving force to reduce all mass transfer resistances of the MB and CR dyes molecules between the aqueous and solid phase of the adsorbent [25].

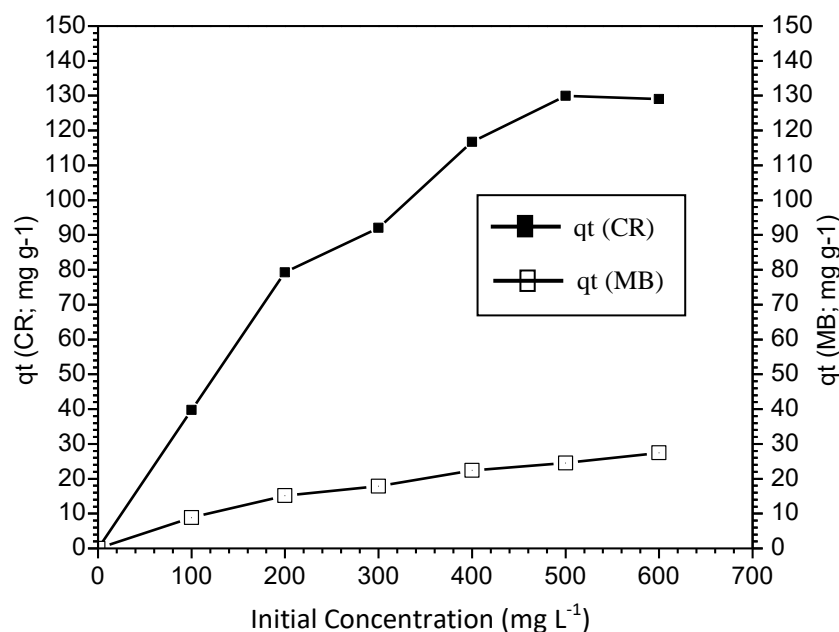


Figure 5. Effect of Initial concentration on congo red and methylene blue dye removal. Conditions: (pH: 6.9, MB: 100 mg.L⁻¹, weight adsorbent: 250 mg, at 30 °C).

3.5. Adsorption isotherms

The interaction between the dyes and the SCFB adsorbent was described by the Langmuir and the Freundlich adsorption isotherms. For the removal of MB and CR by SCFB adsorbent, 25 mL of various dyes concentrations (between 100 and 800 mg L⁻¹) were mixed with 0.250 g sorbent for MB and 0.0625 g sorbent for CR, then stirred at 300 rpm for 120 min at room temperature. The results are shown in Table 2.

From the Langmuir isotherm can be obtained the value of the constants of Q_{max} and R^2 as 128.2 mg g⁻¹ and 1.000 for CR and 35.7 mg g⁻¹ and 1.000 for MB, respectively. Base on the value of maximum adsorption capacity (Q_{max}) can be concluded that adsorption of CR was easier than MB onto SCFB adsorbent.

From the Freundlich isotherm can be determined the constant K_F , n , and R^2 as 0.3937, 0.9976, and 1.000 for CR and 0.0980, 0.9955, and 0.999 for MB, respectively. Base on K_F value shows that the MB and CR adsorption process follows the heterogeneous adsorption process on the surface of SCFB adsorbent which was done through a multi-layer adsorption mechanism. The n values of MB and CR adsorption process close 1, which indicates favorable adsorption of both dyes onto the SCFB adsorbent.

Table 2 Langmuir and Freundlich Isotherm models for CR and MB dyes adsorption on SCFB adsorbent

Dye removal	Langmuir Isotherm			Freundlich Isotherm		
	Q_{max}	B	R^2	K_F	n	R^2
CR	128.21	-1.95×10^{12}	1.000	0.3937	0.9976	1.000
MB	35.714	-4.67×10^{12}	1.000	0.0980	0.9955	0.999

4. Conclusions

Sulfonated carbon derived fishbone (SCFB) can be used to adsorb methylene blue and congo red dyes from aqueous solution. Hydroxyapatite is a major compound that can be found inside the SCFB adsorbent. The SCFB adsorbent has mesopores with the pore radius, pore-volume, and surface area as

9.35 nm, 0.0747 cc g⁻¹, and 15.97 m²g⁻¹, respectively. The kinetic of the MB and CR adsorption process follows the pseudo-second-order model. The maximum removal capacity of both dyes was 128.21 mg g⁻¹ for CR and 35.71 mg g⁻¹ for MB which was calculated from Langmuir isotherm. Base on physical properties and the maximum dye removal capacity, Sulfonated carbon derived fishbone (SCFB) can be recommended to be a good adsorbent to remove dye pollutants from environment especially wastewater.

Acknowledgments

The authors gratefully acknowledge a research grant with contract number: 625/UN17.5/KP/2020 from education faculty and teaching training at Mulawarman University, East Kalimantan Province, Indonesia.

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