Research Article
Adsorption of Cobalt Ion from Aqueous Solution Using Biomaterial of Microalgae *Oscillatoria sp* Isolated from Teluk Jakarta

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Abstract: The adsorption of cobalt onto biomaterial of microalga *Oscillatoria sp* was investigated via batch experiment. Marine alga *Oscillatoria sp* was isolated from Teluk Jakarta Indonesia. The characterization of the functional group with FTIR spectrum showed microalgae have a functional group of O-H, C = O, COO, C-O-C, N-H, C-S, C-H and PO_4^{3-}. Adsorption of cobalt ion was investigated as a function of time, pH, initial cobalt concentration, the dosage of biosorbent, salinity dan shaking. Equilibrium and kinetic adsorption were obtained from the batch experiment. The cobalt adsorption followed the Langmuir and Freundlich, isotherm models. The Freundlich constant (K_f) and n were 0.1186 (mg/g) (L.mol)$^{1/n}$ and 8.43 mg/L, respectively. The maximum adsorption capacity was 4.71 mg/g at pH 8. *Oscillatoria sp* could adsorb cobalt even at a lower concentration, indicating a good affinity for metal. Kinetic studies showed that the adsorption of cobalt ion followed a pseudo-first-order with $k_1 = 1.2 \times 10^{-3}$ min^{-1}.

Keywords: Adsorption, biomaterial, cobalt, *Oscillatoria sp*

INTRODUCTION

The heavy metal contaminant is a problem in the aquatic environment because it can be accumulated in the human body and toxic above the tolerance level (Al-Rub *et al*., 2004). Cobalt is one of the heavy metal that must be reduced in the aquatic system. The higher of Co^{2+} solution was explored to remove Co^{2+} from solution (He *et al*., 2011). High-level cobalt concentration caused DNA damage (Simonsen *et al*., 2012; Leyssens *et al*., 2017). One technique to reduce cobalt contaminants in the aquatic is by adsorption technique using biosorbent. Biosorption is adsorption and accumulation process of pollutants from aqueous solution using the biological materials. Biosorption technique has an advantage in reducing heavy metal ions to a very low level (Feng and Aldrich, 2004). Many types of biomass have been studied for cobalt uptake as lemon peel (Bhatnagar *et al*., 2010), almond green hull (Ahmadpour *et al*., 2009) *Blighia sapida* (Jimoh *et al*., 2012).

Algae is one of the biosorbent in adsorb of toxic heavy metal because of it easy to grow and have a functional group in the wall cell. This functional group including carboxyl, sulfate and phosphate (Ahuja *et al*., 1999; Aravindhan *et al*., 2007). Many studies have shown that algae process high metal binding capacities

(Deng *et al*., 2007). *Oscillatoria sp*, a kind of cyanobacteria microalgae, is widely distributed in eutrophic freshwater and marine environment. Several research has been used *Oscillatoria* as biosorbent to uptake of the heavy metal such as Cu and Zn absorption (Ahuja *et al*., 1997; Ahuja *et al*., 2001; Al-Shammary and Abdulhay, 2016), *Oscillatoria sp* for adsorption of Cd (Azizi *et al*., 2012), Pb (Kumar *et al*., 2011).

In this study, we will explore the potential of microalgae *Oscillatoria sp* for the adsorb of cobalt (II) ion from aqueous solution. Marine microalga *Oscillatoria sp* was isolated from Teluk Jakarta, Indonesia. Effect of pH, adsorbent dosage, the concentration of cobalt, shaking and salinity will be performed in this study. Equilibrium isotherms for the adsorption of cobalt were measured experiment. Adsorption isotherms were determined with Langmuir and Freundlich equation.

MATERIALS AND METHODS

Prepared the material: Microalgae *Oscillatoria sp* obtained from an Indonesian culture collection, LIPI Cibinong. It was grown at 25°C and pH adjusted to 8. The algae were harvest after 14 days of growth. Thereafter, the algal pellet was washed with deionization distillation water and then used for metal

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uptake experiment. Characterization of functional groups from the biosorbent using FTIR. The chemical reagents used in this study are analytical reagent grade. The cobalt solution was prepared by dissolving the $Co(NO_3)_2.6H_2O$ salt in distilled water. The initial ion concentration range 5-50 mg/L. The pH of the solution was adjusted by adding 0.1 M HCl or 0.1 M NaOH. The concentration of cobalt determined using an Atomic Absorption Spectrometer (AAS) (SHIMADZU A6000). Adsorption reading was taken in 240.7 nm.

Adsorption study: The metal uptake experiment was performed in 250 mL Erlenmeyer flask containing 25 mL Co 50 mg/L and 0.25 g biosorbent. The solution becomes to 50 mL with added of demineralization water. The experiment was carried out in batches in different condition of time, concentration, pH, amount of biosorbent, etc. The biosorbent with a known weight was left in contact with 50 mL of cobalt solution (5-50 mg/L) at 150 rpm. The mixture was shaken for 60 min. The parameter adsorption consist of variation of contact time (30-120 min), dosage of biosorbent (0.1-0.6 g), initial concentration of cobalt (5-50 mg/L), shaker (50-200 rpm), pH (3-8) and salinity (0-30 g/L). Thereafter supernatant liquid was filtered and the concentration of cobalt was determined by AAS. The adsorbed quantities of cobalt ion were evaluated using the following equation:

$$qe = \frac{(Co-Ce)V}{W} \tag{1}$$

where,

qe = The amount or concentration of cobalt adsorbed onto the unit amount of microalgae *Oscillatoria sp* (mg/g)
Co = The initial concentration of cobalt (mg/L)
V = The volume of solution (L)
w = The weight of biosorbent (Liu *et al*., 2010; Jeppu and Clement, 2012)

The adsorption percentage of cobalt was adsorbed by biosorbent used the equation below:

$$Adsorption \ (\%) = 100 \ \frac{(Co-Ce)}{Co} \tag{2}$$

where,

Ce = Cobalt concentration in solution
Co = The cobalt initial concentration

Adsorption isotherms: The Langmuir and Freundlich models were studies for equilibrium state. The Langmuir equation was shown below:

$$\frac{Ce}{qe} = \frac{1}{q_{mon}.K_l} + \frac{1}{q_{mon}}.Ce \tag{3}$$

$$\ln q = \ln k + \frac{1}{n}\ln C \tag{4}$$

where,

Ce = The solute concentration (mg/L) at equilibrium
qe = The amount of solute at equilibrium (mg/g)
q = Mon related to adsorption capacity
K = Langmuir constant

The Freundlich equation is an empiric model based on heterogeneous adsorption (Boudrahem, *et al*., 2011):

$$qe = kf \ Ce^{1/n} \tag{5}$$

$$\log q_e = \log Kf + \frac{1}{n}\log Ce \tag{6}$$

Where Kf is the Freundlich constant indicated the adsorption intensity.

Kinetic study: In a different measuring flask, 25 mL of cobalt 50 ppm (known concentration) and a known amount of adsorbent was taken periodic shaking. The solution was filtered and evaluated by atomic absorption spectrophotometer. The controlling mechanism of the metal adsorption process was studied by fitting first or second-order kinetic models. The linearity first-order kinetic model was shown in the below equation:

$$\log(qo - qt) = \log qe - \frac{k1}{2.003}t \tag{7}$$

Where qt is the amount of adsorbate at time t (mg/g), qe is the adsorption capacity at equilibrium (mg/g) k1 is the pseudo-first-order rate constant (min^{-1}) and t is the contact time (minute). The linearity second-order kinetic model is given as:

$$\frac{t}{qt} = \frac{1}{K_2 q^2} + \frac{1}{q_e}t \tag{8}$$

Where k2 is the equilibrium rate constant of pseudo-second-order adsorption (g mg^{-1}. min^{-1}).

RESULTS AND DISCUSSION

Characterization of biosorbent: Characterization of biosorbent was done using FTIR analysis. FTIR spectra of biosorbent *Oscillatoria sp* is shown in Fig. 1. IR spectroscopy has been the method of choice for studying structure and interaction of molecules with identified of functional group (Banyay *et al*., 2003). The identification of functional group from *Oscillatoria sp* can be seen in Table 1. The stretching vibration of C-H indicated the methyl group and usually found in organic compounds (Coates, 2006). The peak of C-H stretching usually occurs below 3000 cm^{-1}. The peaks 1510-1450 is an aromatic stretch (C=C) and 850 cm^{-1} is C-H aromatic (Coates, 2006). Biosorption of metal ion depends on the component and functional group of the biosorbent. This component including cellulose,
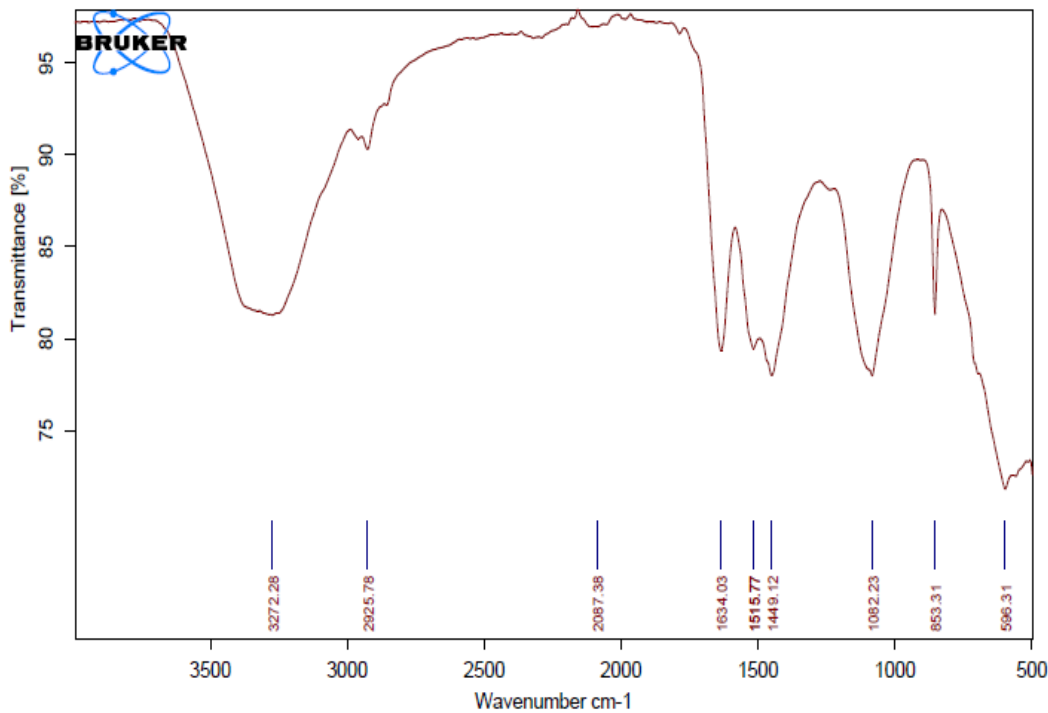
Fig. 1: FTIR analysis of *Oscillatoria sp*

Table 1: Identification of functional group of *Oscillatoria sp*

Wavenumber (cm⁻¹)	Functional group	Chemical group
3272	O-H	Alcohol
2925	O-CH₃, C-H	Hydrocarbon
2087	C-H, N-H, C=O	Hyrocarbon, amine, carbonyl
1634	C-C	Hydrocarbon
1515	C-H	Hydrocarbon
1449	C-H, COO	Hydrocarbon, carboxylate
1082	C-N, C-O-C	Amine
853	PO₄³⁻, C-O-P	Phosphates
596	C-S, mineral	Sulfur, Anorganic compounds
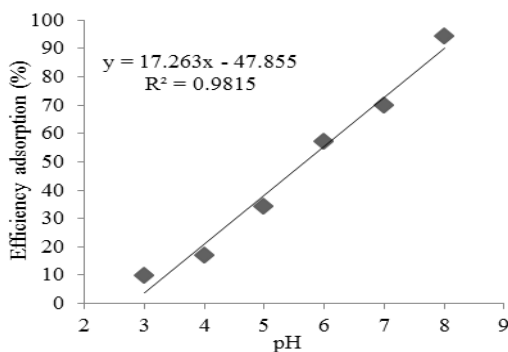
Fig. 2: Effect of pH on the cobalt adsorption into *Oscillatoria sp*.

oxygen, nitrogen, sulfur or phosphorus (Wang and Chen, 2009). The most important of these groups including carboxyl, carbonyl, amine, amide, thiol and phosphonate (Volesky, 2007).

Adsorption study: The cobalt sorption is depended on pH solution. The effect of initial pH on cobalt sorption capacity was studied at 25 mg/L cobalt initial concentration and the result is shown in Fig. 2. The uptake of cobalt in the pH range of 2-8 was determined in this experiment.

Figure 2 shows the relationship between pH and cobalt absorption efficiency by *Oscillatoria sp*. Biosorbent dosage of 0.25 g, the initial concentration of cobalt is 25 ppm and the volume of solution is 50 mL. An increase in pH caused an increase in the amount of cobalt absorbed. There is a linear correlation between pH and adsorption efficiency with a correlation of 0.9815 and equation $y = 17.263x - 47.855$. The maximum efficiency is obtained at pH 8 with the adsorption of 23.58% and adsorption capacity of 4.71 mg/g. The pH solution can affect of metal-binding sites between cobalt and biosorbent. The cell wall ligands are closely associated with hydronium ion at the low of pH (Al-Rub *et al*., 2004). The increase of pH resulted in an increase in biosorption level because of influences of negative surface charge of the functional group. At the low pH occurred the competition between protons and metal ions in the adsorption process (Feng and Aldrich, 2004).

Shaking is carried out to homogenize the solution and regulate the process of absorption of cobalt by *Oscillatoria sp*. The stirring range is carried out with variations of 50-250 rpm. The effect of shaking on cobalt adsorption by *Oscillatoria sp* can be seen in Fig. 3. Based on the experiment, the optimum stirring was
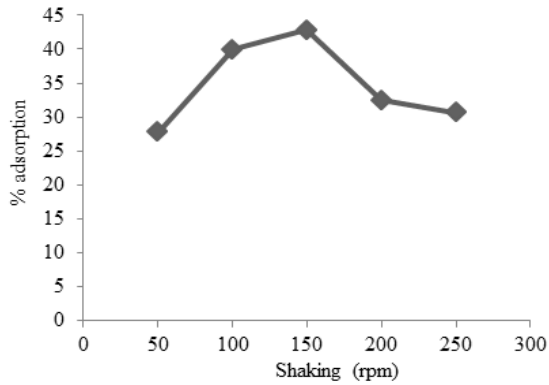
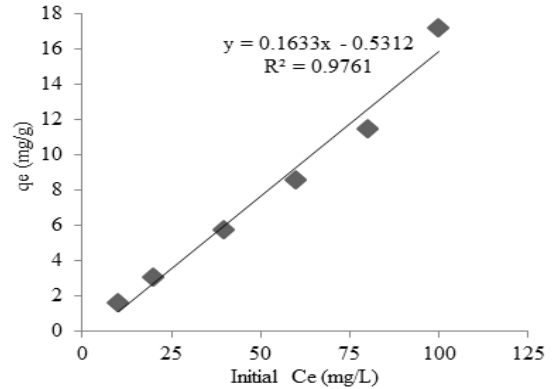Fig. 3: Effect of shaking on the cobalt adsorption into *Oscillatoria sp.*

Fig. 4: Effect of salinity on the cobalt adsorption into *Oscillatoria sp.*

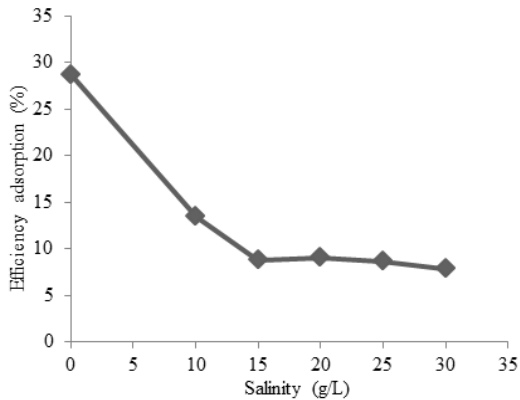Fig. 5: Effect of concentration for the uptake of cobalt by *Oscillatoria sp*
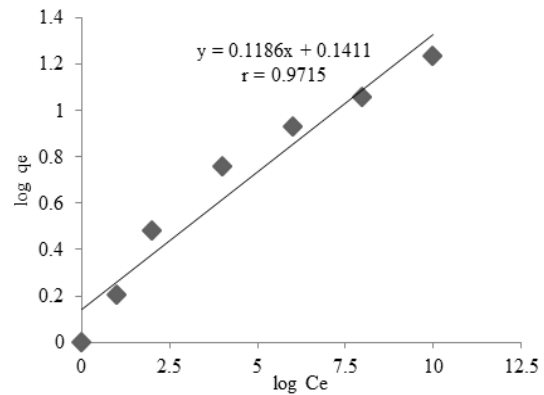

Fig. 6: Freundlich adsorption isotherm

Fig. 7: Langmuir adsorption isotherm

obtained at 150 rpm with an adsorption efficiency of 41.81% and absorption capacity of 2.14 mg/g.

Variation of salinity ion solution from 0-30 g/L. Figure 4 shows the greater the salinity, the smaller of cobalt absorbed by *Oscillatoria sp.* The optimum absorption was obtained in salinity = 0 with optimum efficiency is 28.72% and absorption capacity of 1.43 mg/g. Analytical isotherms equation such as Langmuir and Freundlich isotherms are widely used for modeling adsorption data (Jeppu and Clement, 2012). According to the Langmuir model, sorption occurs uniformly on the active site of the sorbent and once a sorbate occupies a site. These model isotherms can be seen in Fig. 5 to 7.

Figure 5 shows the effect of initial cobalt concentration on adsorption capacity onto *Oscillatoria sp.* The result showed a linear correlation between the initial cobalt concentration and absorption capacity with $R^2 = 0.976$ and equation y = 0.1633x-0.5312. The adsorption isotherm showed the adsorption molecule between the solid and liquid phase on the equilibrium state (Hameed *et al.*, 2007). The applicability of the isotherm equation is compared with the correlation coefficient.
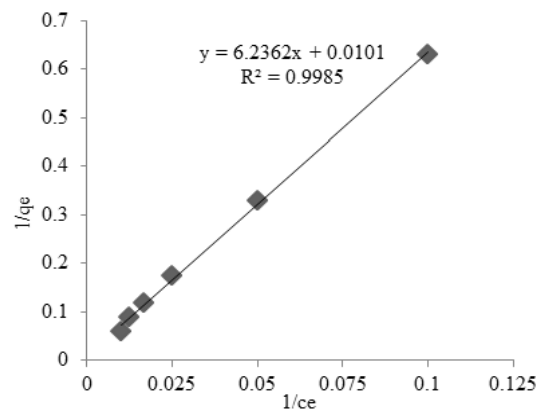
In the Freundlich model, the cases linear plots were obtained which reveal the applicability of this isotherm on cobalt adsorption process (Mittal *et al.*, 2007). The condition experiment was done in pH = 5, the amount of adsorbent = 2.5 g and time of 60 minutes. The correlation shown linear with r = 0.9715 and equation of y = 0.1186x + 0.1411. The linear plot in Ce vs log qe shows that the adsorption of cobalt onto *Oscillatoria sp* follow the Freundlich isotherm model. The Freundlich
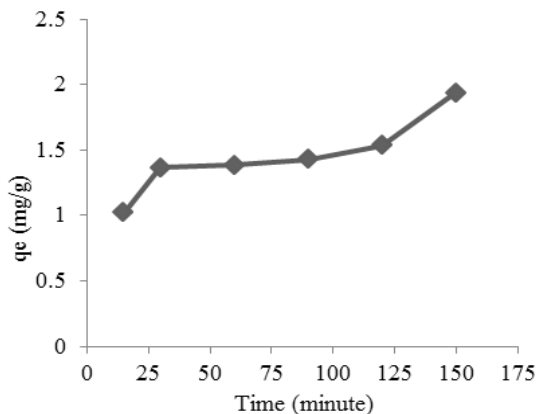
Fig. 8: Adsorption kinetic of cobalt on *Oscillatoria sp*

Fig. 9: Effect of adsorbent dosage for the adsorption of cobalt

adsorption isotherm was also applied for the adsorption of cobalt onto *Oscillatoria sp*. Freundlich constant kf and n were found to be 0.1186 $(mg/g)(L.mol)^{1/n}$ and 8.43 mg/L, respectively.

Optimum adsorption capacity (qm) biosorbent of cobalt to adsorb of cobalt according to Langmuir model was 6.24 mg/g. The slope and the intercept is 6.24 mg/g and 0,01 L/mg, respectively, that it indicated Q max and b. The Langmuir parameters can be used to knowing the affinity between the biosorbent and adsorbate. It can be used to suggests of the adsorption process is monolayer (Kalavathy *et al*., 2005; Ahalaya *et al*., 2010). The linear isotherm model is an alternative mathematical approach to predict the overall adsorption behavior (Chen, 2015).

Kinetic of adsorption: The kinetic parameters were calculated by monitoring the effect of contact time, amount of adsorbent and concentrations of adsorbate solution on adsorption of cobalt. Figure 8 shows the effect of contact time on cobalt absorption by *Oscillatoria sp*. The increase in contact time shows the greater of cobalt absorbed. The optimum contact time is obtained by incubation for 120 min with an absorption capacity of 1.9338 mg/g. In can be inferred that the cobalt could ion could be adsorbed with a short time by using of *Oscillatoria sp*.

Figure 9 shows the effect of adsorbent dosage in cobalt adsorption by *Oscillatoria sp*. The algae dosage was 0.25 g and the initial concentration of Co^{2+} ion was approximately 25 mg/L. The experiment shows increasing biosorbent dose increasing of cobalt adsorption in solution. The dose of biosorbent in the range of 0.1-0.6 g with the amount of adsorbent is 0.2983-0.3712 g. This adsorption involved in the mass transfer of ions from aqueous into the surface of biosorbent (Liu *et al*., 2010).

The kinetics of adsorption describes the rate of cobalt ions uptake on *Oscillatoria sp* microalgae and this rate control by the equilibrium time. The kinetic model of cobalt adsorption can be seen in Fig. 10. The kinetic model indicates the behavior of the adsorbent in
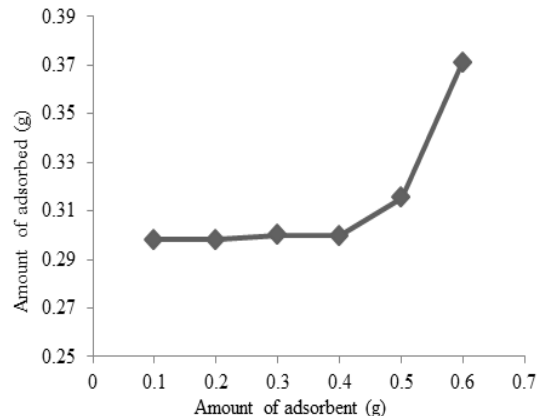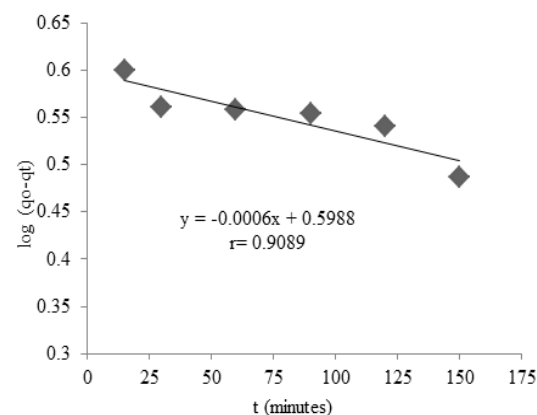

Fig. 10: The kinetic model of cobalt adsorption

the adsorption process (Aravindhan *et al*., 2007). The first-order rate, constant (k_1) and qe were determined from the slope and intercept of the plot (qo-qt) versus time contact. Kinetic studies showed that the adsorption followed a pseudo-first-order. The first-order rate constant k_1 can be found in the experiment was 1.2×10^{-3} min^{-1}.

CONCLUSION

The experimental result shows that microalgae of *Oscillatoria sp* is an alternative for the removal of cobalt was depend on contact time, pH, adsorbent dosage and initial cobalt concentration. Analysis of functional group from biosorbent shows the peaks of hydroxide, carboxyl and carbonyl ions. This functional group is an important role in the biosorption of cobalt ion. The adsorption models of cobalt ion with *Oscillatoria sp* followed the Langmuir and Freundlich isotherms. The kinetic rate shows the pseudo-first-order.

ACKNOWLEDGMENT

CONFLICT OF INTEREST

No potential conflict of interest was reported by the authors.

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