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» Mean-Median based Noise Estimation Method using Spectral Subtraction for Speech Enhancement Technique
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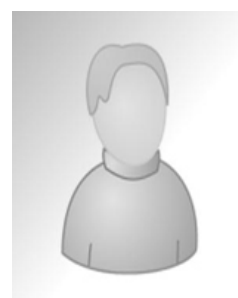
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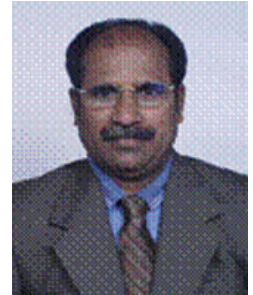
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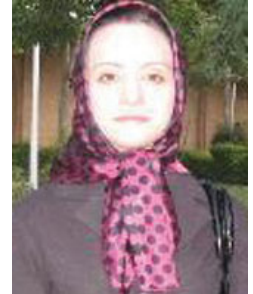
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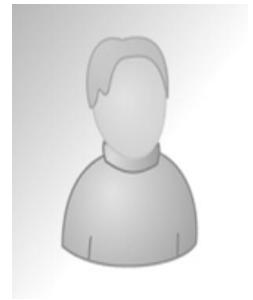
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Removal of Manganese from Well-Water on Pasuruan, East Java, Indonesia Using Fixed Bed Cation Exchanger and Prediction of Kinetics Adsorption

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Abstract

Objectives: Testing of a cation exchanger based water treatment apparatus and an Amberlite IR 120 Na resin medium to reduce the manganese content in the well-water is proposed. **Methods/Statistical Analysis:** Testing was done by well-water treatment in a fixed bed cation exchanger in continuous flow. The variables used were the resin mass and flow rate and its effect on the manganese concentration in the outflow of the equipment. Manganese content was analyzed by Atomic Absorption Spectrophotometry (AAS) method. The isothermal adsorption equation was tested by the Freundlich and Langmuir equations. **Findings:** The result of this research showed Amberlite resin IR 120 Na adsorbed manganese ion was about 96.3-98.9%; the optimal resin mass about 20 grams with a flow rate about 0.04 L.s⁻¹ when viewed from an economic point. Resin absorption power to manganese increases with decreasing flow rate and increasing resin mass. Freundlich equation with constant $n = 0.6539$ and $K_f = 4.6644$ with correlation coefficient 0.7957. Langmuir equation with a constant $A_s = -0.0927$ and $K_b = -6.3820$ with a correlation coefficient -0.4314. **Application/Improvements:** Cation exchanger using Amberlite IR 120 Na resin media capable of remove manganese in well-water with efficiency > 96% and resin can be regenerated again.-

Keywords: Cation Exchange, Isothermal Adsorption, Removal Manganese, Spectrophotometry Method, Water Treatment

1. Introduction

The content of ions and elements in ground water have varies for different locations. They can be affected by water processing, soil erosion processing, and anthropogenic sources (for example mining industrial, smelting of iron ore, steel, and iron production, or waste water disposal^{1,2}. The content of manganese in water³ is about 0.0004 until 0.2 mg.L⁻¹. Based on World Health Organization, the content of manganese in the water⁴ has maximum about 0.1 mg.L⁻¹. Generally, in Indonesia there is Well-water which consists of manganese above the maximum water requirements. Based on Regulation of Indonesia Health Minister⁵, the standardize of clean water contains maximum manganese about 0.5 mg.L⁻¹. Well-water which

containing large enough of manganese, the water colour will be blackish yellow after contact with air and smelling. This water will make blackish spotted on the clothes if the people use this water to wash the clothes⁶. This water also makes black spotted to the toiletries. Manganese shape in the water usually Mn (II) labile, particulate Mn (IV) and Mn (IV) hydroxide⁷. Manganese is a powerful oxidizing agent. If the water contains manganese into the body, this water has a potential to interfere human healthy. There are few effects which affected by manganese in the water, like disorder of mucous membranes, esophagus, manganism, or Parkinson disease, bone disorder, osteoporosis, perthe's disease, cardiovascular disorders, liver, reproductive disorders and mental development, hypertension, hepatitis, posthepatic cirrhosis, hair color changes, obe-

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sity, skin problems, cholesterol, neurological symptoms, and epilepsy^{8,9}. Manganese toxicity usually progressive and irreversible, the discovery of Mn exposure biomarker is growing imperatively¹⁰.

There are few procedures are able to do to decrease the content of toxic substances in water. There are precipitations¹¹, adsorption¹², membrane process¹³⁻¹⁵, and electrolytic method¹⁶. Pretreatment in the adsorption process is aeration or oxidation process. Pretreatment in adsorption process is aeration or oxidation process. In aeration process Mn ions change into Mn ions with higher oxidation numbers and form precipitate. Furthermore, this precipitate is filtered by sedimentation process or filtration process. If the content of manganese is high enough, it can be used as ion exchanger process.

Several researchers have proven that exchanger ions were good enough to remove heavy metals and toxic materials in the water¹⁷. The advantages of exchanger ions are saturated resin that can be regenerated and water flow systems during flexible process, either batch or continuous¹⁸. In exchanger ions can be used resin from natural or synthetic¹⁹⁻²¹. Al-Wakeel et al in 2015 examined the efficiency of manganese removal from solution using chitosan resin (G@Chs). The processing was done by batch system. Adsorption was optimal in pH 6 and the contact time was 150 minutes²². The research conducted by Wakeel et al²² got adsorption efficiency of manganese that was high enough (96.4%), but the research object was artificial sample, not Well-water. This research would refine the previous research that was the use of Amberlite resin IR120 Na which has been shown adsorption efficiency and high enough cation exchange for lead (Pb), which was about 99% in batch system with contact time about 4 hours²³. This research would also refine the previous research which used Well-water sample taken from Kebonagung, Purworejo sub-district, Pasuruan, East Java, Indonesia.

2. Materials and Methods

2.1 Materials and Resin Characteristics

The materials used were well-water, Amberlite resin IR 120 Na, and aquadest. Well-water sample was taken from Kebonagung, Purworejo sub-district, Pasuruan, East Java, Indonesia and the well depth was 42 meters. Amberlite IR 120 Na is strong acid cation exchange resin with the chemical formula $[\text{SO}_2\text{NaC}_6\text{H}_4\text{CHCH}_2]$

$\text{CHCH}_2\text{C}_6\text{H}_4\text{CHCH}_2$. Properties of Amberlite resin IR 120 Na shown in the Table 1.

Table 1. Properties of amberlite resin IR 120 Na

Physical Form	Amber spherical beads
Matrix	Styrene divinylbenzene copolymer
Functional group	Sulfonate
Ionic form as shipped	Na ⁺
Total exchange capacity	≥ 2.00 eq/L (Na ⁺ form)
Moisture holding capacity	45 to 50% (Na ⁺ form)
Shipping weight	840 g/L
Particle Size	
Uniformity coefficient	≤ 1.9
Harmonic mean size	0.600 to 0.800 mm < 0.300
Maximum reversible swelling	mm 2% max Na ⁺ → H ⁺ ≤ 11%

2.2 Tools and Installation Management

The tools used were pump, plastic jug, water container, porcelain cup, and analytical balance. The processing installation is shown in Figure 1.

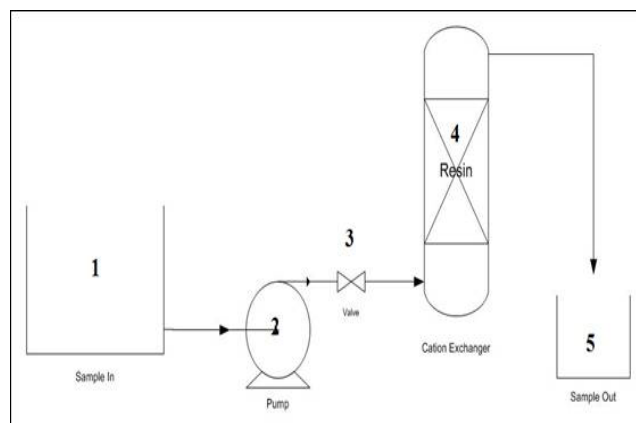


Figure 1. Installation of cation exchanger process.

Explanation:

1. Water container.
2. Pump.
3. Valve.
4. Resin reservoir (Fixed Bed). and
5. Water-storage shelter.

The high pool fixed bed ion exchange was 30 cm, the diameter was 4 inch, and screen strainer was 60 meshes.

2.3 Research Procedure

This research procedure was started from taking the sample, analyzing of initially water quality, weighing of resin,

measuring of pH and Well-water temperature, processing of Well-water, analyzing of water processed, managing of data analysis result, and formulating of Freundlich and Langmuir equation. The weight of resin were 20 grams, 60 grams, 80 grams, and 100 grams, each of them was 3 pieces. In this research, the processing system in a continuously was using 302°K water temperature. The variables used were resin mass and flow rate. There were four resin mass variables; 20 grams, 60 grams, 80 grams, 100 grams. For flow rate, there were three variables, such as 0.02 L.s⁻¹; 0.03 L.s⁻¹; and 0.04 L.s⁻¹. The analyzing of manganese degree in the water was using atomic absorption spectrophotometry method.

2.4 Manganese Removal

Amberlite resin IR 120 Na has been removed the manganese by absorption and ions exchanger process. The efficiency (η) of Amberlite resin 120 Na in manganese removal was calculated with eq. (1).

$$\eta = \frac{C_i - C_o}{C_i} \times 100\% \quad (1)$$

η is resin efficiency in manganese removal (%), C_i is manganese degree in the Well-water before processing (mg.L⁻¹), and C_o is manganese degree in the Well-water after processing (mg.L⁻¹).

2.5 Isothermal Absorption

Absorption processes through ions exchanger reaction mechanism, physical adsorption, electrolytes molecule adsorption, the formation of complexes between central ions and functional groups, and the formation of hydrates in the surface or in the pores of the adsorbent. The amounts of metal which can be absorbed by resin are the function from two concentrates; metal and temperature. The amount of Mn absorbed is determined as concentration function in the constant temperature. It can be explained in the isothermal adsorption equation, between Freundlich and Langmuir. Freundlich isothermal equations were used to describe the resin adsorption characteristics which used in solution or waste water treatment²⁴.

The adsorption power of Amberlite resin 1RR 120 Na to Mn can be described in the equations of Freundlich and Langmuir. These two equations described the effi-

ciency of resin adsorption to Mn from Well-water. In this study, it is not known exactly the oxidation of manganese ions in the water. However, most manganese in the natural water is in the form of mainly Mn (II) ions, particulate Mn (IV), and Mn (IV) hydroxide (2). Manganese ions adsorption in the surface of Amberlite resin IR 120 Na can be evaluated using equation isotherm adsorption. Water treatment process in this study was using continue system. Therefore, the data taken to isotherm adsorption evaluate was the smallest flow rate, was 0.02 L.s⁻¹ with the assumption the condition processes have had steady state. Isothermal adsorption is a system in balance condition between manganese concentrate in the Well water and manganese concentrate in resin at a certain temperature²⁵. Isotherm adsorption is able to give important information about absorption strength and maximum absorption capacity as it helps predict the condition and predict the operating experiment condition is more optimal. The characteristic of isotherm adsorption of Amberlite resin 120 Na to manganese can be evaluated using Freundlich and Langmuir equation.

2.6 Freundlich Equation

Freundlich Equation is shown in (2).

$$\frac{x}{m} = K_f \times C_e^{1/n} \quad (2)$$

$$\frac{x}{m} = K_f \times C_e^{1/n}$$

$\frac{x}{m}$ Is Mn amount was absorbed per unit resin mass (mg.L⁻¹.g⁻¹), C_e is Mn concentration in adsorbate after the desorption process (mg.L⁻¹), K_f and n are empirical constant. Constants K_f and n can be searched by eq. (3).

$$\log \frac{x}{m} = \log K_f + \frac{1}{n} \log C_e \quad (3)$$

2.7 Langmuir Equation

Langmuir isothermal equation is shown in (4).

$$\frac{c}{q} = \frac{1}{K_b A_s} + \frac{c}{A_s} \quad (4)$$

A_s and K_b are coefficient, q is Mn weight which adsorbed per unit resin mass (mg.L⁻¹.g⁻¹), and c is Mn concentration in the Well-water after absorbed (mg.L⁻¹).

3. Result and Discussion

This study is studied about the effect the changing of resin mass and flow rate to the efficiency of Amberlite resin IR 120 Na for decreasing Mn content from well water. Besides, this study would study about isotherm adsorption kinetics of Amberlite resin IR 120 Na to manganese contained in well-water.

3.1 Beginning Analysis of Well Water

Well water that would be processed into clean water analyzed its characteristics based on parameters in Regulation of Indonesia Health Minister⁵. The result of the initial analysis of the Well-water samples are presented in Table 2 shows that the maximum manganese content in clean water is 0.5 mg / l, whereas the manganese content of well water is 2.72 mg / l. this proves that manganese content in well water is not yet qualified as clean water.

Table 2. Comparison of well-water specifications to clean water specifications

Parameter	Degree	Maximally*
Smell	No smell	No smell
Taste	Normal	Normal
Temperature	26.1°C	Water Temperature \pm 3°C
TDS	433 mg/L	1500 mg/L
Turbidity	6.73 NTU	25 NTU
Colour	0 Pt/Co	50 Pt/Co
pH	7.64	6.5 – 9.0
As	< 0.00006 mg/L	0.05 mg/L
Fe	0.87 mg/L	1 mg/L
F	0.46 mg/L	1.5 mg/L
Cd	< 0.001 mg/L	0.005 mg/L
CaCO ₃	332 mg/L	500 mg/L
Cl ⁻	40 mg/L	600 mg/L
Cr ⁶⁺	< 0.026 mg/L	0.05 mg/L
Mn	2.72 mg/L	0.5 mg/L
Nitrate	0.15 mg/L	10 mg/L
Nitrite	< 0.01 mg/L	1 mg/L
Hg	<0.000008mg/L	0.001 mg/L
Se	< 0.00007 mg/L	0.01 mg/L
Zn	0.072 mg/L	15 mg/L
CN	< 0.01 mg/L	0.1 mg/L
SO ₄	< 4.2 mg/L	400 mg/L
Pb	< 0.002 mg/L	0.05 mg/L

Surfactant	< 0.05 mg/L	0.5 mg/L
Organic	< 7.6 mg/L	10 mg/L
Coliform	9 Col./100 mL	10 Col./100 mL

*Regulation of Indonesia Health Minister⁵

3.2 The Efficiency of Amberlite Resin IR 120 Na

The analysis of manganese content in Well water which has been processed using Amberlite resin IR 120 Na with two variables; resin mass and flow rate (Q) described in Table 3 showed manganese content from Well water which has been processed with Amberlite resin IR 120 Na. Table 3 presents manganese content from Well water treated using Amberlite resin IR 120 Na has fulfilled the requirements of clean water based on Minister of Health Regulation Number 32/2017. The ability of Amberlite resin IR 120 Na in doing manganese absorption in the water counted from efficiency formula in equation(1). The efficiency of Amberlite resin IR 120 Na in decreasing manganese shown in Table 4.

Table 3. Analysis of manganese content from well-water after processed with amberlite resin IR 120 Na

Resin Mass (g)	Manganese Content (mg.L ⁻¹)		
	Q1=0.02 L.s ⁻¹	Q2=0.03 L.s ⁻¹	Q3=0.04 L.s ⁻¹
20	0.07	0.07	0.1
60	0.06	0.06	0.09
80	0.05	0.05	0.09
100	0.03	0.03	0.09

Table 4. The efficiency of Amberlite resin IR 120 Na in doing manganese absorption in well-water

Resin mass (g)	Efficiency of Amberlite resin IR 120 Na (%)		
	Q1=0.02 L.s ⁻¹	Q2=0.03 L.s ⁻¹	Q3=0.04 L.s ⁻¹
20	97.43	97.44	96.32
60	97.79	97.79	96.69
80	98.16	98.16	96.69
100	98.90	98.90	96.69

Table 4 has shown manganese degree from Well water after processed with resin and the variables of resin mass and flow rate. Table 4 presented flow rate 0.02 L.s⁻¹ resin efficiency between 97.43 – 98.90%; in flow rate 0.03 L.s⁻¹ resin efficiency among 97.44 – 98.90%; and in flow rate 0.04 L.s⁻¹ resin efficiency about 96.32 – 96.69%.

Efficiency of Amberlite resin IR 120 N a adsorption to manganese with resin mass and flow rate variables. This research was learning about the influence of flow rate to Mn content in the water treatment and the efficiency of resin adsorption. There were three flow rate variables used; 0.02 L.s⁻¹; 0.03 L.s⁻¹; and 0.04 L.s⁻¹. Table 3 showed well water skipped by resin in the pool with continuous system has met the requirements of clean water based on Regulation of the Minister of Health Number 32/2017. The lower flow rate got, the lower the content of ion Mn²⁺ in the water treatment got. It proved the lower flow rate got, the higher the efficiency of resin adsorption to Mn was higher. Resin efficiency to flow rate 0.02 L.s⁻¹ and 0.03 L.s⁻¹ were same, about 97,4-98,9%. The correlation between the resin mass and efficiency of resin for the flow rate 0.02 L.s⁻¹, 0.03 L.s⁻¹, 0.04 L.s⁻¹ was about 0.9535, 0.9264, and 0.8783. The highest correlation was achieved at the flow rate 0.02 L.s⁻¹.

This study was also learning the influence of resin mass to manganese content of water treatment and the efficiency of resin adsorption. There were four resin mass variables used. They were 20 grams, 60 grams, 80 grams, and 100 grams. Table 3 showed manganese content in the water treatment has been requirement of clean water based on Minister of Health Regulation Number 32 /2017. The larger the resin mass, the lower the manganese content of the Well water. In flow rate 0.02 L.s-1 and 0.03 L.s-1, resin mass optimal was 60 grams. Figure 1 presented flow rate 0.02 L.s-1 dan 0.03 L.s-1, the higher resin mass, the higher the efficiency of resin adsorption to Mn in the Well water. The efficiency of resin adsorption in resin mass condition 100 grams was 98.90%. In flow rate 0.04 L.s-1, the higher resin mass, the higher the efficiency of resin adsorption to Mn, but the mass of 60 grams, there was no more increases the efficiency of adsorption. Optimal resin efficiency at 60 grams was 96.69%. Table 4 showed that the correlation between the flow rate and efficiency of resin for the resin mass 20 g, 60 g, 80 g, 100 g was about 0.8660, 0.8660, 0.9993, 0.9387. The highest correlation was achieved at the resin mass 80 g.

The biggest resin efficiency was in resin mass condition 100 grams with flow rate 0.02 L.s⁻¹ and 0.03 L.s⁻¹. That was 98.9%. It proves if the efficiency of Amberlite resin IR 120 Na decreases Mn content in the Well water is higher than the efficiency of chitosan resin which modified with glycine (G@Chs)²² in decreasing Mn content from synthetic sample, about 96.4%.

3.3 Isothermal Absorption

The absorption power of Amberlite resin IR 120 Na to Mn can be described in Freundlich and Langmuir equation. The both equation describe the efficiency of resin adsorption to Mn from Well-water. Freundlich equation is shown in eq. (2) and (3). The graphic to describe Freundlich equation is in Figure 2.

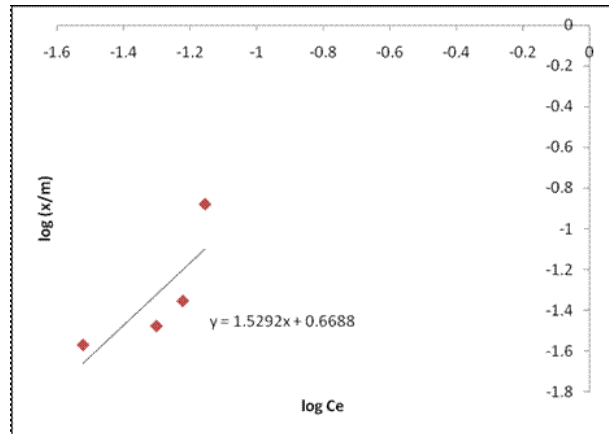


Figure 2. Log (x/m) and log C_e in Freundlich equation.

Figure 2 is a graphic connection between log(x/m) and log C_e. Based on eq. (3) and Figure 2 was gotten (1/n) = 1.5292 and n = 0.6539. Whereas, log K_f = 0.6688 so K_f = 4.6644.

Freundlich equation was obtained from isothermal absorption of Ambrelite resin IR 120 Na to Mn is:

$$\frac{x}{m} = 4.6644 C_e^{1.5292} \quad (5)$$

Correlation coefficient from Freundlich equation was about 0.7957.

Langmuir isothermal equation shown in equation (4). The graphic to describe Langmuir equation shows in Figure 3.

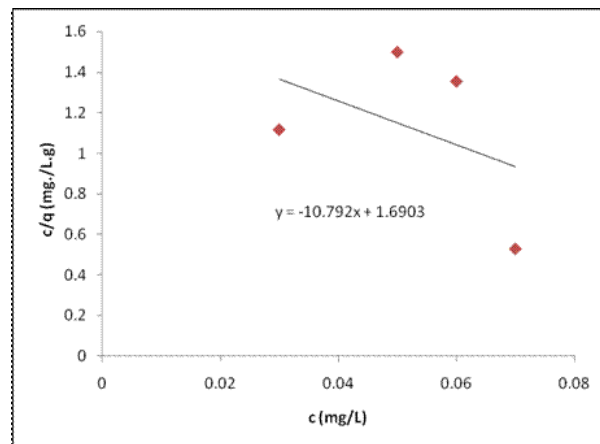


Figure 3. Graphic c/q and c from Langmuir equation.

Figure 3 is a connection graphic between c/q and c . Based on eq. (4) and Figure 3 have gotten as $n = -0.0927$, while $K_b = -6.3820$. The Langmuir equation obtained from the isothermall adsorption of Amberlite resin IR 120 Na to Mn was:

$$\frac{c}{q} = 1.6903 - \frac{c}{0.0927} \quad (6)$$

The correlation coefficient Langmuir equation was about -0.4314 .

Graphic fitting c/q and c from experiments to calculation result based on Freundlich equation and Langmuir equation described in Figure 4.

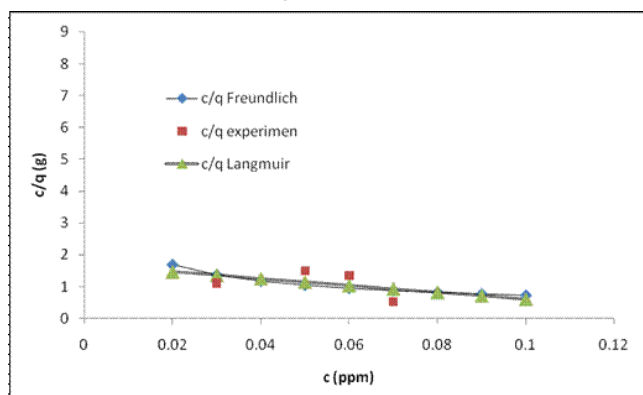


Figure 4. Fitting of c/q and c from experiments to calculation result based on Freundlich and Langmuir equation.

4. Conclusion

The result of this study showed Amberlite resin IRT 120 Na was able to produce manganese in the Well-water and for the efficiency was about 96.3-98.9%. Water treatment has filled the requirements of clean water in Indonesia based on the standard of Regulation of Health Minister. Absorption to Mn (II) can be optimal with resin mass operating system about 20 - 100 grams and the flow rate was 0.02 - 0.04 L / s. The lower flow rate and the higher resin mass got, the higher the efficiency of resin absorption to Mn (II) got. The isothermall from Amberlite resin IR 120 Na to Mn(II) in the Well-water was expressed in Freundlich equation with constanta $n = 0.6539$ and $K_f = 4.6644$; whereas when it was expressed in Langmuir equation with constanta $A_s = -0.0927$ and $K_b = -6.3820$. Correlation coefficient Freundlich equation of 0.7957 and it included has a strong correlation. While the Langmuir equation coefficient of -0.4314 and it included a moderate correlation.

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6. References

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