

Assesing efectiveness of sodium metabisulfite for treatment of coal tar wastewater

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Abstract. The coal gasification activity produces tar wastewater which can cause serious environmental problems. Research that has been conducted to treat wastewater requires a high cost with a long process. For this reason, it is necessary to find another method that is relatively cheaper and a simple process. that is by adding chemicals. This study aims to determine cheap and effective chemicals for treating tar wastewater. The chemicals used are calcium hypochlorite (CHC), hydrogen peroxide (H₂O₂), sodium bisulfite (SBS), and sodium metabisulfite (SMBS). The method used is by characterizing the sample, determining the most dominant factor in dissolving tar with the response surface methodology (RSM), and measuring the levels of total organic carbon (TOC), pH, and radioactivity before and after the addition of chemicals. The sample used consisted of two samples named Y and Z. The results showed that the main contents in Y and Z samples were total phenol 28.1 and 37mg/kg, poly aromatic hydrocarbon (PAH) 0.2 dan 0.5 mg/kg, benzene 0.004 dan <0.001mg/kg, and toluene 0.006 dan 0.002 mg/kg respectively. By using the RSM method it is known that among the factors of volume, speed and time, the most dominant factor in dissolving tar is volume. The use of SMBS can reduce (TOC) optimally. The reduction efficiency of total phenol, total PAH, benzene, and toluene reaches 100%. By this process, pH and radioactivity values meet the requirements set by the government of the Republic of Indonesia.

Keywords: gasification, wstewater, oxidation, and environment

1. Introduction

Coal is one of the energy that is still a mainstay. When compared to other fuels such as petroleum and natural gas, the coal is more easily stored and transported [1, 3, 4, 5, 7, 13, and 14]. Conversion of coal by various processes to produce a combustible gas mixture is called coal gasification. This process not only aims to produce gas to be used as fuel, but also serves to produce other gases that can easily be converted into chemicals or as petrochemical reserves of economic value [6, 10, and 11].

The coal gasification process also produces tar. The nature and composition of coal tar is very complex, black-colored liquid with high viscosity. The composition consists of phenol, polycyclic aromatic hydrocarbons (PAHs) and heterocyclic compounds. The components and properties of tar



depend on the temperature of the gasification and the carbon content of the coal used [15]. Although tar is not soluble in water, polar compounds in tar such as phenol are soluble [17]. The organic matter consumes the dissolved oxygen (DO) from water [18]. The value of DO decreases. Consequently the organism in the water will die from lack of oxygen. The DO concentration have been used as primary indicator of water quality [2]. Total organic carbon (TOC) is widely-employed indicator for estimating the total amount of organic compounds in water samples [8]. TOC is a kind of quickly comprehensive indicators for water quality and able to fully reflect kind of pollutants in water [16]. The compounds can be a source of water pollutants. Therefore, good management off tar should be done.

Coal tar wastewater treatment has treated by using activated sludge followed by ozonation process has long been studied. Efficiency of chemical oxygen demand removal is 41% [19]. Other processing is by using a mediator-less, membrane-less microbial fuel cell. pH decreased from 7.8 to 7.0 during 24 days, whereas 88% of chemical oxygen demand, 57% of sulfate, and 41% of sulfur were removed. Besides concentration of aluminum, silver, barium, copper, iron, molybdenum, sulphur, strontium, phenol, and 2-methyl phenol decreased [9]. Although the results of these processes are good, but require equipment that is relatively expensive. Besides that the processing is long enough. Therefore need to develop a method that is relatively short and does not require expensive equipment.

One way to reduce the level organic material is the oxidation process using oxidizing agents. Organic matter will be oxidized to carbon dioxide and water. There are several kinds of oxidizing agents, such as $\text{Ca}(\text{OCl})_2$ (called CHC), H_2O_2 , NaHSO_3 (called SBS) and $\text{Na}_2\text{S}_2\text{O}_5$ (called SMBS). Chemical formula SMBS is $\text{Na-O-(S=O)-O-(S=O)-O-Na}$. SMBS is a compound in the form of crystals or white powder, is easily soluble in water and slightly soluble in alcohol. Sodium metabisulfite has a molecular weight of 190.12 g/mol. The density of this compound is 1.2-1.3 kg/L and its melting point is 150 °C. In addition to wastewater treatment, SMBS is also referred to as food additives, sanitization and cleaning agents [12].

In addition to the cheap price of these chemicals easily obtained. All of these chemicals will be tested for their effectiveness in reducing levels of organic content, in this case TOC. So this study aims to determine which compounds are most effective in reducing TOC levels in tar water. With the recognition of these compounds, tar waste water can be managed properly through a simple and relatively inexpensive treatment process. Of course, ultimately it is expected that environmental damage can be avoided.

2. Materials and Methods

2.1. Materials

The tar samples used in this research are from the gasification activities of R&D Center for Mineral and Coal Technology, Palimanan, Cirebon, Indonesia. While the chemicals used are H_2O_2 , $\text{Ca}(\text{OCl})_2$ (CHC), NaHSO_3 (SBS), and $\text{Na}_2\text{S}_2\text{O}_5$ (SMBS). Laboratory apparatus used are shaker (JISICO) and DO meter (Orion Star).

2.2. Method

Two sample of tar as much as ± 10 kg taken in different times from its place of storage. The first sample (named Y) was taken in June 2016 and the second (named Z) in December 2016. Tar is then characterized to know the composition. Response surface methodology is done to determine the most dominant factor in dissolving the dissolved material in tar. Some water then added into 10 g tar and shaken by using shaker (Table 2.1 and 2.2). The addition of water is done to a minimum of DO. The 200 mL fluid was filtered then added 10%, 20%, 30%, 40% and 50% oxidizing agents, namely CHC, H_2O_2 , SBS, and SMBS then stirred for 15 min. Solutions before and after the addition of chemicals were tested for pH, total organic carbon, organic compounds and their radioactive elements. The efficiency before and after processing of some organic parameters is calculated by the formula:

$$\text{Efficiency (\%)} = ((A-B) / A) \times 100\%$$

Where A = concentration of substances before treatment, and B = concentration of substances after treatment

Table 2.1.Experiment variable Y and Z.

Experiment	Volume of water, ml (Factor 1)	Speed of shake, rpm (Factor 2)	Time, minutes (Factor 3)
1	20	100	120
2	20	100	30
3	20	25	120
4	20	25	30
5	180	100	120
6	180	100	30
7	180	25	120
8	180	25	30

3. Results and Discussion

3.1. Results

After several gasification experiments, 2 samples of tar were taken in different times. The content of phenol in the tar is highest among the other compounds (Table 3.1). The tar samples used in this research are from the gasification activities of R&D center for mineral and coal technology, Palimanan, Cirebon, Indonesia. While the chemicals used are H_2O_2 , $\text{Ca}(\text{OCl})_2$ (CHC), NaHSO_3 (SBS), and $\text{Na}_2\text{S}_2\text{O}_5$ (SMBS). Laboratory apparatus used are shaker (JISICO) and DO meter (Orion Star).

Table 3.1.The organic composition of Y and Z samples.

Parameter	Unit	Samples	
		Y	Z
BTEX			
Benzene	mg/kg	6.29	17.6
ethyl benzene	mg/kg	<0.002	<0.002
Toluene	mg/kg	21.4	66.2
xylene total	mg/kg	51.5	192
Polycyclic aromatic hydrocarbons, PAH total	mg/kg	17.32	33.333
Naphtalene	mg/kg	3.1	2.2
Acenaphthylene	mg/kg	0.7	0.1
Acenaphthene	mg/kg	0.4	0.003
Fluorene	mg/kg	2.5	4.83
Phenantrene	mg/kg	3.1	7.6
Antracene	mg/kg	2.7	8.6
Fluoranthene	mg/kg	0.71	0.09
Phyrene	mg/kg	1,25	3.14
benzo(a)anthracene	mg/kg	0.86	3.3
Chrysene	mg/kg	0.05	0.16
benzo (b)fluoranthene	mg/kg	0.16	0.09

benzo (k) fluoranthene	mg/kg	0.1	0.04
benzo (a) pyrene	mg/kg	1.06	1.65
indeno (1,2,3-c,d)pyrene	mg/kg	0.22	0.66
dibenz (a,h) anthracene	mg/kg	0.06	0.04
benzo (g,hi) perylene	mg/kg	0.35	0.83
Total PCBs	mg/kg	27.4	16.2
Total Pesticides	mg/kg	1.25	2.4
Phenol	mg/kg	5,340	18,800
2,4,6-trichlorophenol	mg/kg	656	476
2,4-dichlorophenol	mg/kg	6,510	14,000
2,4-dimethylphenol	mg/kg	1,510	2,460
2-chlorophenol	mg/kg	699	572
Pentachlorophenol	mg/kg	23,700	10,700
TPH	mg/kg	56,600	65,820
≤C9	mg/kg	1,600	4,120
C10-C19	mg/kg	18,300	26,100
C20-C30	mg/kg	25,600	23,500
≥C31	mg/kg	11,100	12,100

3.2. Dissolutions of tar in water

Treatment of tar has done by adding water to the tar. The purpose of this treatment is to remove a soluble compound with water. Water will dissolve some of the polar compounds present in the tar. The solubility of compounds in water is influenced by several factors such as water volume, stirring and time. For that is done in the laboratory test for the most dominant factor can be known. The test results of Y and Z samples showed that the most influential factor for dissolving substances in tar was factor 1 or water volume. The total values of each sample of y and z are 0.659 and 0.669 (Table 3.2). The result equation for the sample y and z are:

$$Y \text{ yield} = 2.914 + 0.659 \text{ factor } 1 + 0.099 \text{ factor } 2 + 0.381 \text{ factor } 3 + 0.019 \text{ factor } 1.2 - 0.074 \text{ factor } 1.3 + 0.556 \text{ factor } 2.3$$

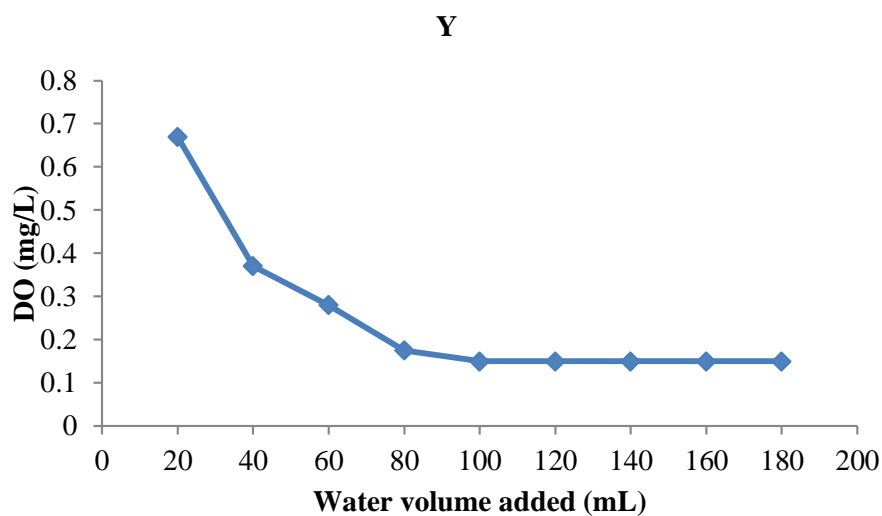
$$Z \text{ yield} = 2.879 + 0.669 \text{ factor } 1 + 0.079 \text{ factor } 2 + 0.419 \text{ factor } 3 + 0.024 \text{ factor } 1.2 - 0.096 \text{ factor } 1.3 + 0.529 \text{ factor } 2.$$

Table 3.2. Calculation of the most dominant factor in influencing the value of DO.

Experiment	Intercept	YSample			Result	Factor 1.2	Factor 1.3	Factor 2.3
		Factor 1	Factor 2	Factor 3				
1	1	-1	1	1	3.47	-1	-1	1
2	1	-1	1	-1	1.2	-1	1	-1
3	1	-1	-1	1	1.95	1	-1	-1
4	1	-1	-1	-1	2.4	1	1	1
5	1	1	1	1	4.43	1	1	1
6	1	1	1	-1	2.95	1	-1	-1
7	1	1	-1	1	3.33	-1	1	-1
8	1	1	-1	-1	3.58	-1	-1	1
Total	2.914	0.659	0.099	0.381		0.019	-0.074	0.556

Experiment	Intercept	ZSample			Result	Factor 1-2	Factor 1-3	Factor 2-3
		Factor 1	Factor 2	Factor 3				
1	1	-1	1	1	3.35	-1	-1	1
2	1	-1	1	-1	1.18	-1	1	-1
3	1	-1	-1	1	2.1	1	-1	-1
4	1	-1	-1	-1	2.21	1	1	1
5	1	1	1	1	4.46	1	1	1
6	1	1	1	-1	2.84	1	-1	-1
7	1	1	-1	1	3.28	-1	1	-1
8	1	1	-1	-1	3.61	-1	-1	1
Total	2.879	0.669	0.079	0.419		0.024	-0.096	0.529

The value of DO indicates the amount of oxygen contained in the solution. The result of tar dissolution test with the addition of some water volume indicates that the DO value in the solution will decrease (Figure 1). This is due to the increasing amount of substances dissolved by the addition of water. The more dissolved substances the value of DO will decrease. The optimum condition was achieved when adding 100 ml of water to 10 g of tar sample. Under these conditions the value of DO looks constant at its lowest point.



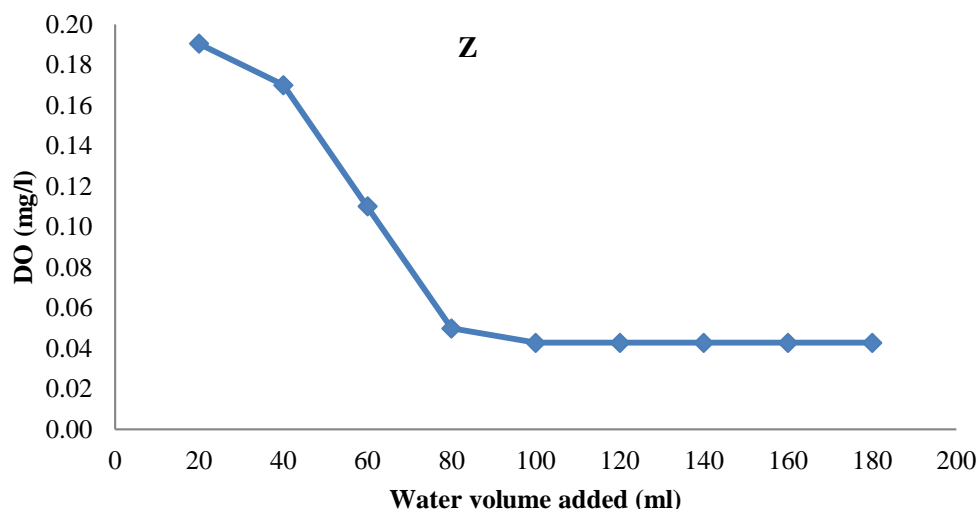
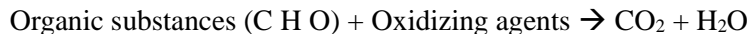


Figure 1. A decrease in the value of do due to the addition of water to both samples

3.3. Reduction of TOC

The total value of organic carbon (TOC) shows the number of organic carbon compounds in the sample. This parameter is used as reference efficiency in tar waste water treatment. The decreasing level of TOC shows that the processing is getting better. With the addition of oxidizing agents, organic substances will oxidize to CO_2 and H_2O . The general reactions that occur are:



The addition of H_2O_2 relatively lowers the levels of TOC. This occurs due to the existing wastewater solution neutral atmosphere. The oxidizing properties of H_2O_2 will get bigger in acidic atmosphere. However, the addition of acid is not done in this experiment considering it will increase the cost of further processing to neutralize the pH with lime (CaO). The use of CHC is only up to 20% only. This is due to the emergence of a lot of gas in the addition of these chemicals. Chemical reactions that occur not only produce CO_2 gas, but also produced gas Cl_2 . As a result raises a new environmental problem, namely how to handle gas Cl_2 . Of course this is not expected. The third period elements in the periodic system (ie sodium (Na), magnesium (Mg), aluminum (Al), silicon (Si), phosphorus (P), sulfur (S), chlor (Cl), and argon (Ar)), has a stronger oxidation power to the right. so CHC actually has the strongest oxidation power so it will be most effective in reducing TOC levels. But considering the problem of the emergence of Cl_2 gas which will pollute the environment, CHC cannot be applied.

S has a stronger oxidation power than P but is smaller than Cl. The reduction values of P, S, and Cl are respectively, -0.276, -0.508, and +1.358. Therefore, SMBS is the main choice in reducing TOC levels in tar waste water. Actually SMBS and SBS are compounds that can function the same because if the SMBS is dissolved in water it will turn into SBS according to the following reaction:



When compared to H_2O_2 , CHC, and SBS the use of SMBS in the same amounts turned out to show a more effective reduction in TOC levels. Efficiency reached 33.83% for Y samples and 60% for Z samples (Figure 3.2).

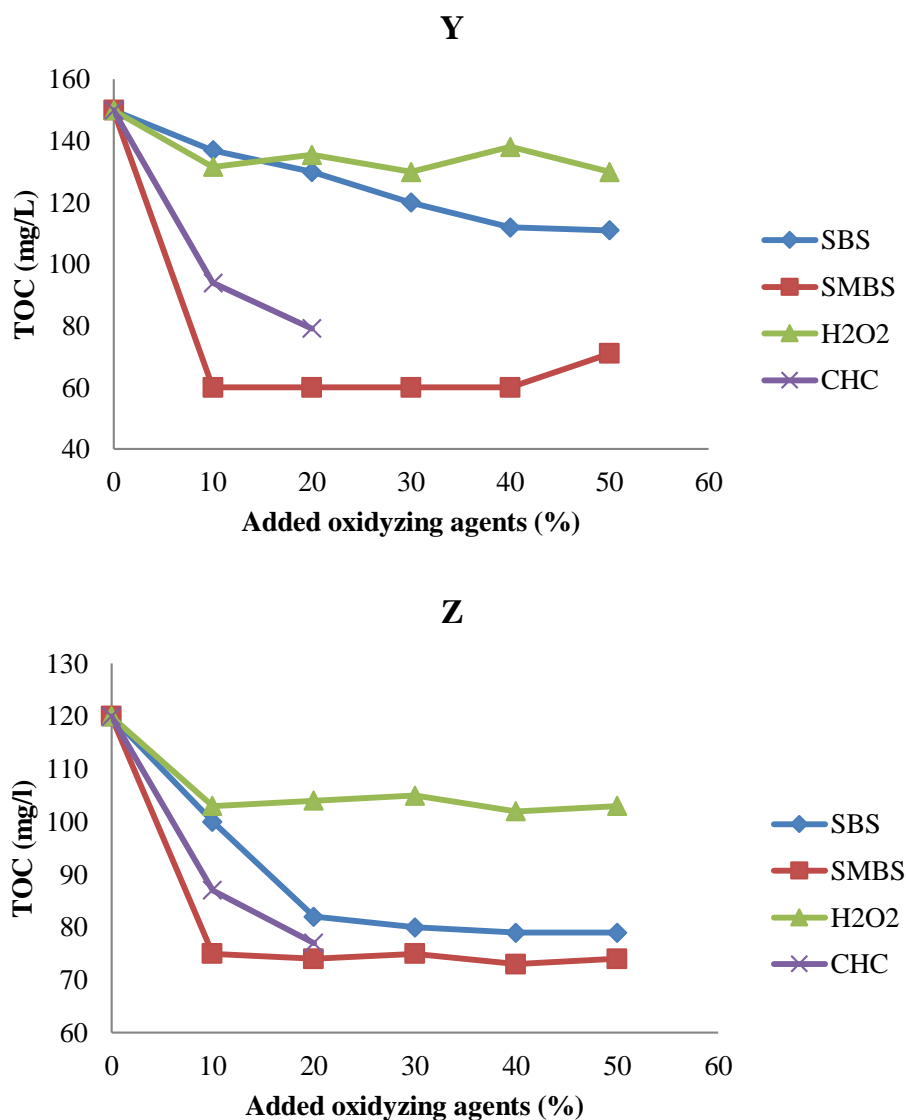


Figure 3.2. Comparison of TOC reduction by using various chemicals.

Y and Z test results using 40% and 20%, respectively, and SMBS 10% resulted in significant reductions. Total phenol was reduced by 100% in both samples. Total PAH reduction efficiency in Y sample reaches 100% using SMBS 30%, but only 50% if using SBS 40%. While in Z sample, the efficiency of PAH reduction reaches 100%. Toluene in both samples can also be reduced in concentration. Its reduction efficiency reaches 100% (Tables 3.3 and 3.4). With prices on the international market in 2018 of around US\$ 0.385 / kg, the production costs needed to process 200 mL of tar waste water are around US\$ 0.0077.

Table 3.3. The results of the Y tar samples were tested using SBS 40% and SMBS 10%.

Parameter	Before	After added SBS	After added SMBS
total phenol	28.1	<0.001	<0.001
PAH total	0.2	0.1	<0.1
benzene	0.004	<0.001	<0.001
ethyl benzene	<0.001	<0.001	<0.001
toluene	0.006	<0.001	<0.001
xylene total	<0.003	<0.003	<0.003
p,m-xylenes	<0.001	<0.001	<0.001
m,p-xylene	<0.002	<0.002	<0.002

Table 3.4. The results of the Z tar sample sampling test using SBS 20% and SMBS 10%.

Parameter	Before	After added SBS	After added SMBS
total phenol	37	<0.001	<0.001
PAH total	0.5	<0.001	<0.001
benzene	<0.001	<0.001	<0.001
ethyl benzene	<0.001	<0.001	<0.001
toluene	0.002	<0.001	<0.002
xylene total	<0.003	<0.003	<0.003
p,m-xylenes	<0.001	<0.001	<0.001
m,p-xylene	<0.002	<0.002	<0.002

The acidity (pH) test results showed that relatively few changes before and after addition of SBS and SMBS (Table 3.5). This is because both SBS and SMBS is a salt that is neutral. So the reaction will not change the pH value much. Acidity level has met the quality standard in regulation of Environment Minister of republic of Indonesia, No. 82 of 2001 on wastewater management, that is 6-9.

Table 3.5. Test fluid pH before and after addition of SBS and SMBS

Sample	Before	After added SBS	After added SMBS
Y	6.69	6.73	6.75
Z	6.71	6.74	6.77

3.4. Radioactivity test

The existence of radioactive elements can be a threat to the environment. The properties of radioactivity were analyzed by precipitation and observed using low alpha beta counter (low background counter) referring to Indonesian standard, SNI ISO 9696: 2009 and SNI ISO 9697: 2009. The result of Y radioactive test showed gross A of 814.60 ± 35.89 and gross B smaller than instrument detection limit that is used is <0.02 Bq/kg. The Z sample demonstrated a small radioactive gross A concentration (<0.01 Bq/kg). But it contains gross B of 139.47 ± 28.93 Bq/kg.

The concentration of radioactive elements in both samples (Table 3.6) also shows that the presence of radioactive substances is still below the intervention level referring of rule of the Head of the nuclear energy body of Republic of Indonesia, No. 9 of 2009 about Intervention Against Exposure Derived From Technologically Enhanced Naturally Occurring Radioactive Material. Thus, the dissolved radioactive material is still below the intervention level. The addition of SBS produces sulfite compounds which exhibit lower activity properties (Table 3.7). It appears that there is a

decrease in the concentration of all radioactive elements except potassium. This is because these elements become elements of the elemental of sodium. However, the concentration of potassium is still below its intervention level of 10.000 Bq/L.

Table 3.6. Radioactive concentrations of tar samples

Sample	Y	Z
²³⁰ Th	6.12 ± 0.74	<1.52
²³⁴ Th	<0.15	<0.15
²³⁸ U	<1.20	<1.20
⁴⁰ K	0.65 ± 0.09	1.60 ± 0.26
²¹⁰ Pb	5.65 ± 0.65	<1.00
²²⁶ Ra	0.32 ± 0.04	0.11 ± 0.001
²²⁸ Ra	0.40 ± 0.06	<0.04
²²⁸ Th	0.36 ± 0.04	0.26 ± 0.03

Table 3.7. The concentration of radioactive element of wastewater after the addition of SBS 30%

Sample	Y	Y (+SBS)	Z	Z (+SBS)
²³⁰ Th	<1.52	<1.52	<1.52	<1.52
²³⁴ Th	<0.15	<0.15	<0.15	<0.15
²³⁸ U	<1.20	<1.20	<1.20	<1.20
⁴⁰ K	1.14 ± 0.12	0.63 ± 0.07	0.30 ± 0.03	<0.10
²¹⁰ Pb	5.65 ± 0.65	0.02 ± 0.01	<1.00	<1.00
²²⁶ Ra	0.32 ± 0.04	<0.04	0.68 ± 0.07	0.11 ± 0.01
²²⁸ Ra	0.40 ± 0.06	<0.04	0.28 ± 0.03	<0.04
²²⁸ Th	0.36 ± 0.04	<0.03	0.63 ± 0.02	0.26 ± 0.03

4. Conclusios

The addition of a certain amount of water to the tar is the most influential factor in dissolving a soluble substance in tar compared to the shaking and time factor. SMBS is more effective for treating tar compared to H₂O₂, CHC, and SBS. Some measurement parameters such as TOC, total phenol and PAH are reduced drastically. The value of pH and radioactive properties have met the requirements set forth in the laws of the Republic of Indonesia. Further research will be directed to sulfate treatment. One method that is easy to do is by the method of precipitation. Sulfate ions can be precipitated as calcium sulfate by adding lime.

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