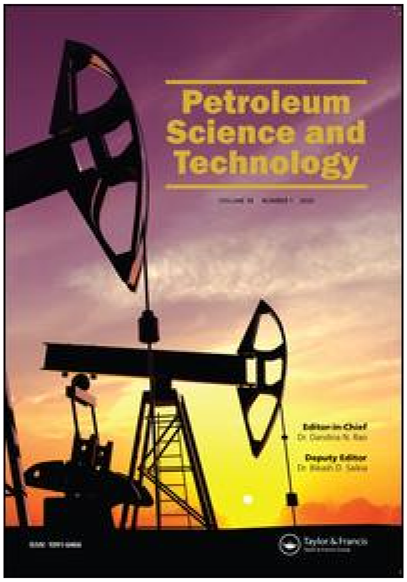

Desulphurisation of high-sulphur petroleum coke by hot NaOH leaching

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Desulfurization of High-Sulphur Petroleum Coke by Hot NaOH Leaching

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Research on efficient use of carbon-originated solid fuels is gaining importance, as the reserve of petroleum is depleting. The production of fuels from coal is being investigated intensively. In some studies, coal/water and coal/liquid fuel mixtures have been tested in internal combustion engines and power plants with promising results.

This study obtain high-purity petroleum coke, which can substitute liquid fuels in the form of mixtures of Petroleum coke /water or Petroleum coke/liquid fuel. Desulfurization of a low ash, high sulphur containing petroleum coke was performed at different leach temperatures, NaOH/petroleum coke ratios and different particle sizes to determine the optimum leach conditions.

Keywords: petroleum coke; desulfurization; particle size distribution; NaOH leaching; petroleum coke-water-slurry

Symbols and abbreviations

kcal/kg: Kilocalories/kilograms

mPa.s: Megapascal. santipoise

mm: Millimeter

h: Hours

M: Molars

°C: Centigrade degrees

ml: Milli liters

CWS: Coal–water–slurry

PCWS: Petroleum coke–water–slurry

Sx: Poly-sulphurs

CMC: Carboxy methyl cellulose

1. Introduction

Petroleum coke is a solid by-product of the petroleum industry that arises while refining crude petroleum. Recently, in addition to high carbon and calorific value and very low ash content, it has been more popular as it is a very inexpensive fuel (Commandré and Salvador 2005; Milenkova et al. 2005; Qihui et al. 2011; Chen et al. 2017; Hojatallah et al. 2018). Production of petroleum coke as a by-product is increasingly becoming higher as the demand for transportation fuels increases, heavier crude oils are used, and environmental regulations are being brought for refined fuels (Marc et al. 2007; Roskill Consulting Group 2007). As they show different characteristics based on their production method, petroleum cokes are used in different fields. For example, they can be used as raw material or as fuel in refineries, cement, steel and aluminum industries (Ruikun et al. 2012; Rambabu et al. 2013). Petroleum cokes, which consist of hydrocarbons, have high carbon content, high calorific value, low ash content and high sulphur content (Chen and Lu 2007; Clements et al. 2012).

Petroleum coke chemically contains sulphur and some trace elements, as well as less volatile substances and ash compared to coal. However, its high sulphur and trace element contents create usage and environment-related problems. With the regulation of the Ministry of Environment, for petroleum coke usage, the dry sulphur content should not be higher than 5%, and the lower thermal value should not be under 7000 kcal/kg (Radenovic and Teric 2010). Sulphur components of petroleum products have harmful effects. For example, it was determined that the sulphur components in gasoline led to rotting in some parts of the engine especially in winter conditions (Speight 2006). When petroleum coke is leached with HCl, 20% of sulphur, and when it is leached with NaOH, more sulphur can be removed (Cheong and Lee 2000; Ibrahim and Morsi 2015).

Slurry fuels, including coal–water–slurry (CWS) and petroleum coke–water–slurry (PCWS), are suspensions of coal or petroleum coke powders in water (Wang et al. 2018). By the development of the coal-water slurry (CWS) technology, a new liquid fuel was found by forming petroleum coke and water mixtures. PCWS is a new liquid fuel and has similar flow characteristics to gasoline (Zhao et al. 2008a; Zhao et al. 2008b; Jie et al. 2018). In studies of production of liquid fuel from coal that has been going on for years, coal/water and coal/liquid fuel mixtures were tested in internal combustion engines and electricity power plants, and promising results were reached (N'kpomin et al. 1995; Ugwu and Samson 2014). Coal-water slurries (CWS) are suspensions that contain a high ratio of coal which is formed by fine-ground coal and water. A typical CWS contains 50%–75% coal, 25%–49% water and 1% chemical additives in its structure. A suitable coal-water mixture refers to mixtures that have a viscosity equivalent to that of kerosene at most and does not cause a problem in certain storage and transportation conditions. While mixtures are being prepared, it is desired that their viscosities do not exceed the value of 1000 mPa.s, and their stability is around 21 days (Morrison, Bruce, and Scoroni 1993; Atesok et al. 2002; Boylu, Ateşok, and Dınçer 2005). Coal-water and diesel-coal mixtures have characteristics that can be used in large combustion engines (ship engines, locomotives, electricity generators, etc.) as fuel (Bournival, Pugh, and Ata 2012; Dash et al. 2015).

When petroleum coke is processed with sodium or potassium hydroxide at high temperatures in an oxygenated environment at certain ratios and times, the sulphur that holds on to carbon atoms in the structure of the petroleum coke by weak bonds is separated by clinging to Na or K atoms. As the affinity of carbon against oxygen is higher in an oxygenated environment, the carbon surface is oxidized by forming C–O or C–O–C bonds. After separation from carbon, sulphur forms poly-sulphurs (S^x), and these poly-sulphurs form various compounds with the Na^+ or K^+ ions in the environment (Na_2S, K_2S). This way, sulphur is separated from the petroleum coke. When this mixture is washed with water and dilute acid, the sulphur is taken as a solution with sodium or potassium, and what remains is pure petroleum coke (Cheong and Lee 2000; Holeman and Wiberg 2001).

- Petroleum cokes – S + 2MOH → M_2S + Cokes – O + H_20
- M = Na or K (Cheong and Lee 2000).

This study reduces the sulphur content in petroleum coke originating from Northern America that contains a high amount of sulphur and obtain high-purity carbon that can be used in certain ratios as coal/water or coal/liquid fuel mixtures. In the experiments, the removal of sulphur from petroleum coke was achieved by NaOH leaching at different NaOH/petroleum coke ratios, different coke particle sizes and different temperatures, and it was determined the optimum leaching conditions.

2. Materials and methods

2.1 Material

Petroleum coke samples with a particle size of approximately -100 mm (Figure1) were ground down to under 0.075 mm, 0.063 mm and 0.025 mm by using a jaw crusher and a rod mill. The general flow diagram of the work that was carried out was as shown in Figure 2. Afterwards, leaching experiments were carried out with these samples. Looking at previous studies on desulfurization, NaOH was used to remove the sulphur in the petroleum coke (Cheong and Lee 2000).

[Figure 1 goes here]

2.2 Method

NaOH and petroleum coke were mixed homogenously with a small amount of water addition.

Afterwards, this mixture was kept in a stove at 80°C until the water evaporated. After this mixture, following homogenous mixing, the sample was kept in a muffle furnace at a determined temperature for 2 h. The samples that were taken out of the furnace at the end of two hours were washed firstly with hot water and then with 0.5 M HCl, and again, with distilled water until the pH became around 5–5.5. Afterwards, the leached sample was subjected to chemical analyses. In all tests, the total sulphur amount was determined using a 5E-IRSII Manual IR sulphur analysis device.

[Figure 2 goes here]

3. Results and Discussion

3.1 Determination of the Optimum NaOH/Petroleum coke Mixture Ratio

The results of the chemical analysis on the feeding material are as shown in Table 1. In the first series of tests, it was found the optimum mixture ratio in the leaching tests conducted at 550°C on various NaOH/Petroleum coke mixtures (Figure 4) Table 2 shows the analysis results.

[Table 1 goes here]

[Table 2 goes here]

[Figure 3 goes here]

[Figure 4 goes here]

As shown in Table 2 and Figure 3, the best result was obtained at the 3 NaOH/Petroleum coke ratio. The following temperature tests were continued at this ratio.

3.2 Determination of the Optimum Leaching Temperature

As shown in Table 3 and Figure 5, the best result was obtained at a temperature of 700°C. The S ratio was reduced down to 1.09%.

[Table 3 goes here]

[Figure 5 goes here]

3.3 Determination of the Optimum Petroleum coke particle Size

After the leaching temperature test series, to investigate the effects of petroleum coke particle size on sulphur removal, leaching tests were carried out with samples that were ground under 0.075 mm, 0.063 mm and 0.025 mm at 3 NaOH/Petroleum coke ratio and at a temperature of 700°C. The results of these tests are shown in Table 4 and Figure 6.

[Table 4 goes here]

[Figure 6 goes here]

In this series of leaching tests, it was determined that the sulphur content dropped down to the level of 0.65% in the sample that was ground under 0.025 mm. The lower calorific value of the obtained leaching product was determined as 8285 kcal/kg.

3.4 Determination of the Optimum CMC amount, measuring of the penetration rate and the Viscosity of the Petroleum coke-Water Slurries (PCWS)

The prepared mixtures were stored using 600 ml jars with caps, and at the end of a certain storage time, a glass rod seen in Figure 7 with a length of 30 cm and diameter of 6 mm was dipped into the mixtures, and the distance it covered in the mixture, namely penetration, was determined. The degree of penetration was determined by using the equation below.

$$\text{Penetration\%} = (d_t/d) \times 100 \quad (1)$$

Here, d_t is the distance covered by the glass rod in the mixture in cm, d is the distance that needs to be covered by the glass rod in the mixture (mixture height, cm) (Boylu and Ateşok 2005).

[Figure 7 goes here]

In the penetration measurements, the mixtures with 80% or higher penetration percentages were considered stable mixtures, and the storage times that provided these values were determined as the ideal storage times (Boylu and Atesok 2005).

Viscosity measurements were made with the Branson viscosity device that is shown in Fig 8. The mixing rate was 10 rpm, and the L2 nozzle was used in the viscosity measurements. The results of the measurements made with the Branson viscosity device are shown in Table 4.

[Figure 8 goes here]

As seen from Table 4 the lowest viscosity at an acceptable penetration was obtained at the CMC ratio of 0.01% at 770 mpa.s, the penetration ratio became stable at 90.1% at the end of the 7th day.

[Table 5 goes here]

[Figure 9 goes here]

4. Conclusion

In this study, success was reached in reducing the sulphur content of a high sulphur petroleum coke, which is a petroleum waste, from 5.29% to 0.65% using the method of NaOH hot leaching.

After leaching, the ash contents increased. This increase in ash was due to the loss of volatile compounds from the sample at high temperature. There was a very small amount of decrease in the lower calorific value of petroleum coke after leaching. The calorific depreciation can be associated with the loss of volatile compounds. In 3 series of tests that were carried out, the optimum conditions were determined as the NaOH/petroleum coke ratio of 3 and leaching temperature of 700°C.

In the study, the petroleum coke that was obtained in grain sizes of 0.025 mm, with the lower calorific value of 8285 kcal/kg and contents of 85% C, 1.1% ash, 0.65% S and 9.12% volatile matter had the characteristics to be used in production of very high-quality coal-water and/or coal/liquid fuel slurries. The petroleum coke-water slurries (PCWS) were subjected to viscosity tests at a solid ratio of 30%, at a temperature of 20–25°C and CMC ratios of 0.002, 0.01, and 0.05%, and looking at the seven – day penetration % ratios at these rates, the lowest viscosity value was obtained at the CMC ratio of 0.01% at 770 mpa.s, and the penetration ratio became stable at 90.1% at the end of the 7th day.

The economical usability of carbon that is obtained in a multi-stage process where the methods for grinding, high-temperature caustic soda leaching, washing and filtration are used to substitute liquid fuels is, of course, depends on the costs of liquid fuels. Today, because the oil costs are high, the importance of such innovative fossil solid fuel products will be increased from day to day.

Disclosure statement

The author reports there are no competing interests to declare.

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Table 1. Feeding material chemical analysis results (dry basis).

Table 2. Effects of the NaOH/Petroleum coke mixture ratio at 550°C on Petroleum coke properties (0.075 mm).

Table 3. Effects of leaching temperature at 3 NaOH/Petroleum coke ratio on petroleum coke properties (0.075 mm).

Table 4. Effects of particle size at 3 NaOH/Petroleum coke ratio and 700°C on petroleum coke properties.

Table 5. Results of tests for the determination of the optimum CMC Rate for a stable PCWS.

Figure 1. Crushed Petroleum coke Sample.

Figure 2. General Flow Diagram of the Processes.

Figure 3. Effects of the NaOH/Petroleum coke weight ratio at 550°C on C and S ratios.

Figure 4. NaOH/Petroleum coke mixture samples before thermal processing.

Figure 5. Effects of leaching temperature at 3 NaOH/Petroleum coke ratio on C and S content.

Figure 6. Effect of particle size at 3 NaOH/Petroleum coke ratio and 700°C on C and S content.

Figure 7. Penetration test setup (Boylu and Ateşok 2005).

Figure 8. Viscosity measurement appliance.

Figure 9. Petroleum coke Water.

Table 1. Feeding material chemical analysis results (dry basis).

Ash (%)	Moisture (%)	Volatile Matter (%)	Carbon (%)	Sulphur (%)	Lower calorific value (kcal/kg)
0.97	0.17	11.53	88.23	5.29	8409

Table 2. Effects of the NaOH/Petroleum coke mixture ratio at 550°C on Petroleum coke properties (0.075 mm).

NaOH/Petroleum coke Ratio by Weight (%)	Carbon (%)	Sulphur (%)	Volatile Matter (%)	Ash (%)	Lower calorific value (kcal/kg)
0.5	88.12	5.02	10.05	1.14	8312
1	87.05	4.83	9.34	1.13	8302
2	87.01	4.61	9.12	1.11	8291
3	85.41	4.34	9.58	1.19	8284

Table 3. Effects of leaching temperature at 3 NaOH/Petroleum coke ratio on petroleum coke properties (0.075 mm)

Temperature (^oC)	Carbon (%)	Sulphur (%)	Volatile Matter (%)	Ash (%)	Lower calorific value (kcal/kg)
500	86.20	5.03	9.65	1.05	8315
550	85.41	4.34	9.58	1.19	8284
600	84.12	4.11	8.72	1.20	8212
650	82.15	3.02	8.17	1.23	8058
700	81.50	1.09	8.45	1.32	7987
800	80.50	1.24	8.48	1.36	7884

Table 4. Effects of particle size at 3 NaOH/Petroleum coke ratio and 700°C on petroleum coke properties

Particle size (mm)	Carbon (%)	Sulphur (%)	Volatile Matter (%)	Ash (%)	Lower calorific value (kcal/kg)
-0.075	87.43	1.23	10.05	1.16	8314
-0.063	87.05	1.33	9.74	1.14	8302
-0.025	84.99	0.65	9.12	1.10	8285

Table 5. Results of tests for the Determination of the optimum CMC Rate for a stable PCWS

Weight (%)	CMC (%)	Temperature (°C)	Viscosity (mpa.s)	Penetration Time (Days)	Penetration Rate (%)
30	0	20-25	661	1	100.00
				2	87.12
				3	86.55
				4	84.34
				5	83.27
				6	82.13
				7	79.30
30	0.002	20-25	671	1	100.00
				2	93.18
				3	91.53
				4	90.44
				5	89.52
				6	88.41
				7	83.59
30	0.01	20-25	770	1	100.00
				2	95.12
				3	94.23
				4	94.12
				5	91.32
				6	89.14
				7	90.15
30	0.05	20-25	794	1	100.00
				2	98.27
				3	97.15
				4	97.52
				5	96.14
				6	96.19
				7	95.90
30	0.05	23	794		
	0.05	40	890		
	0.05	60	993		
	0.05	80	980		

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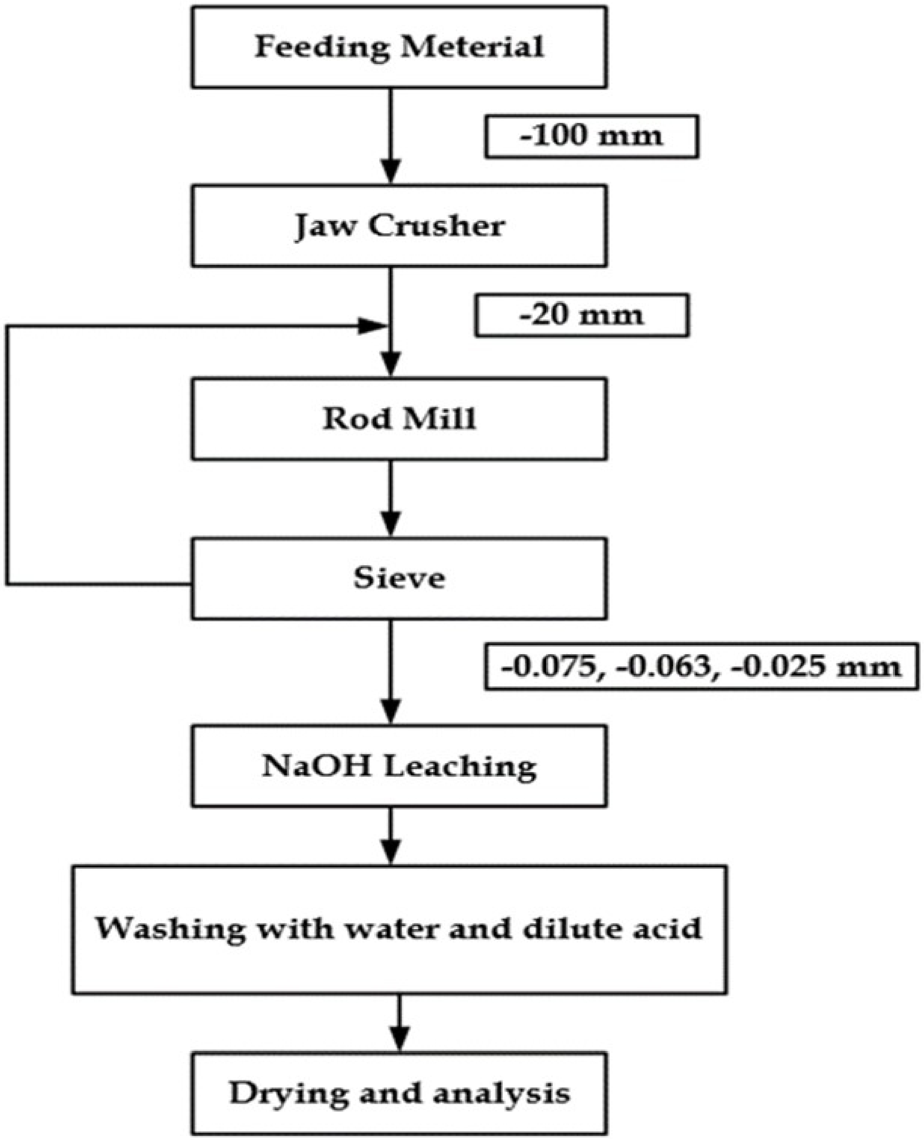

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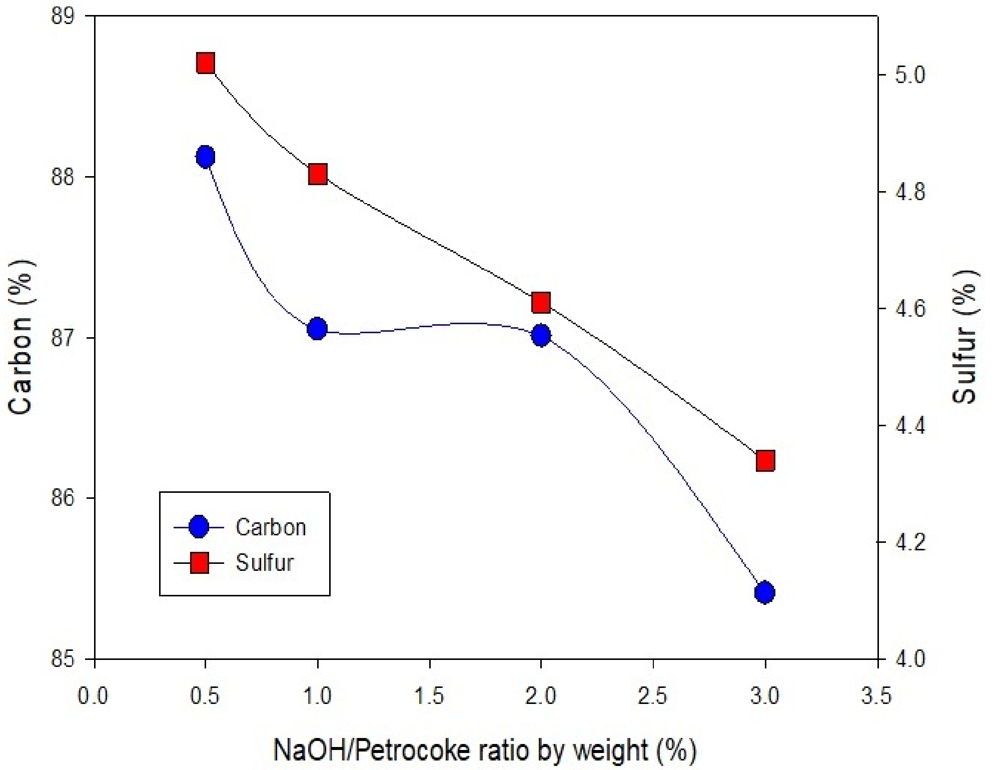

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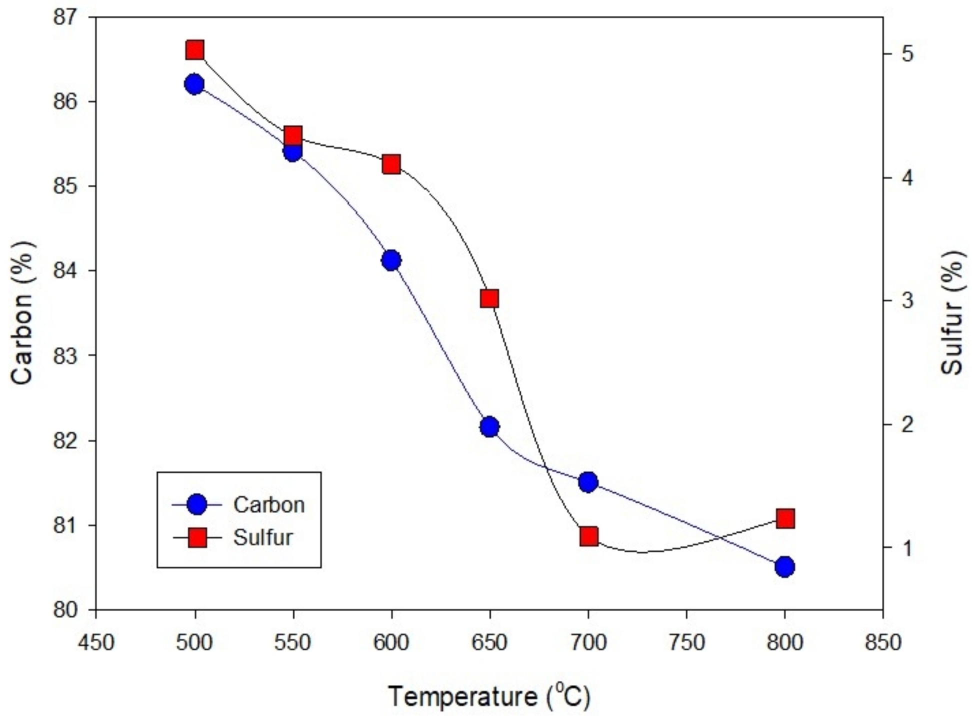

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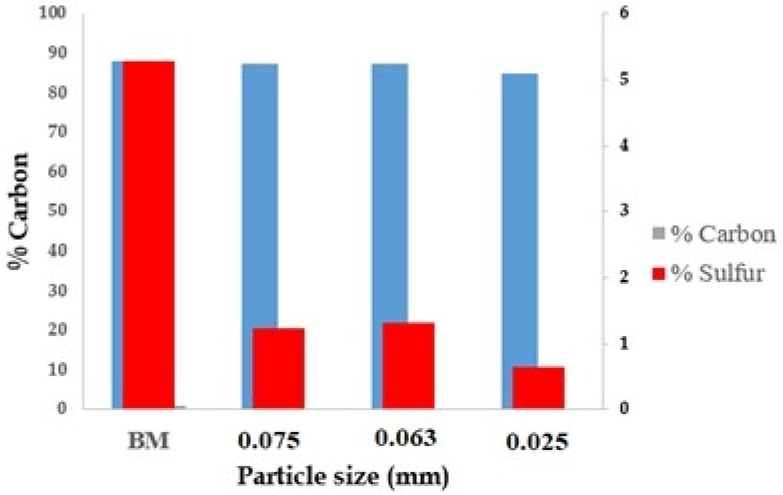

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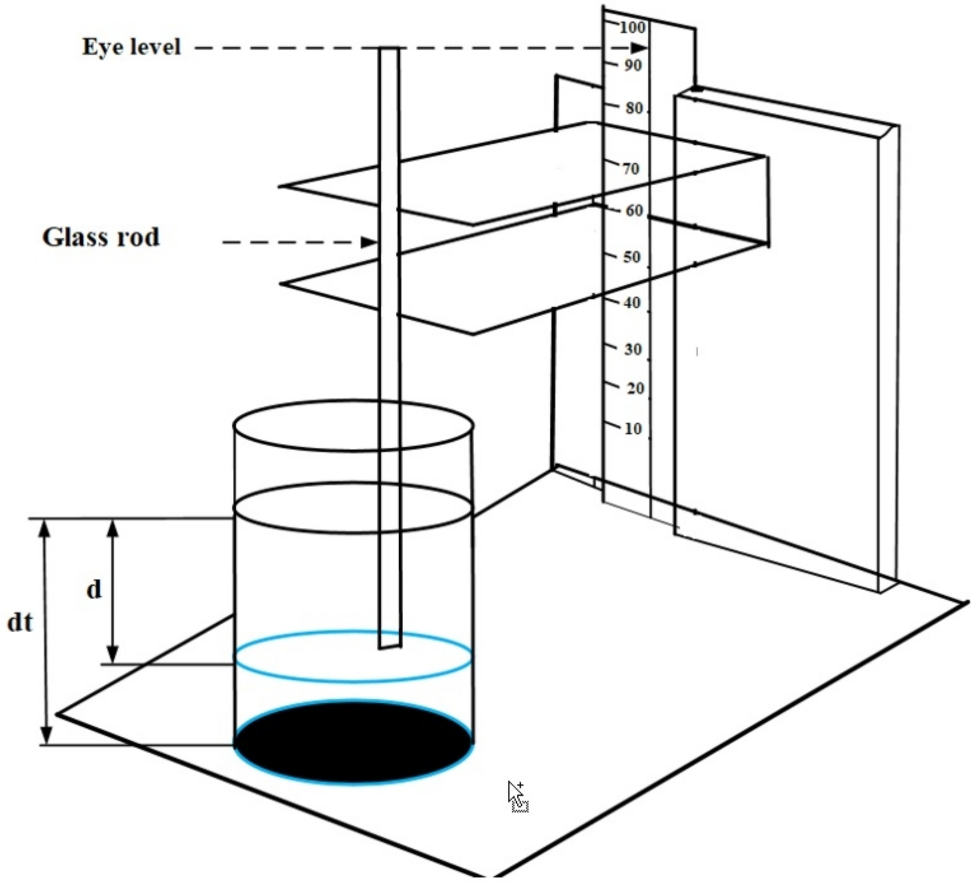

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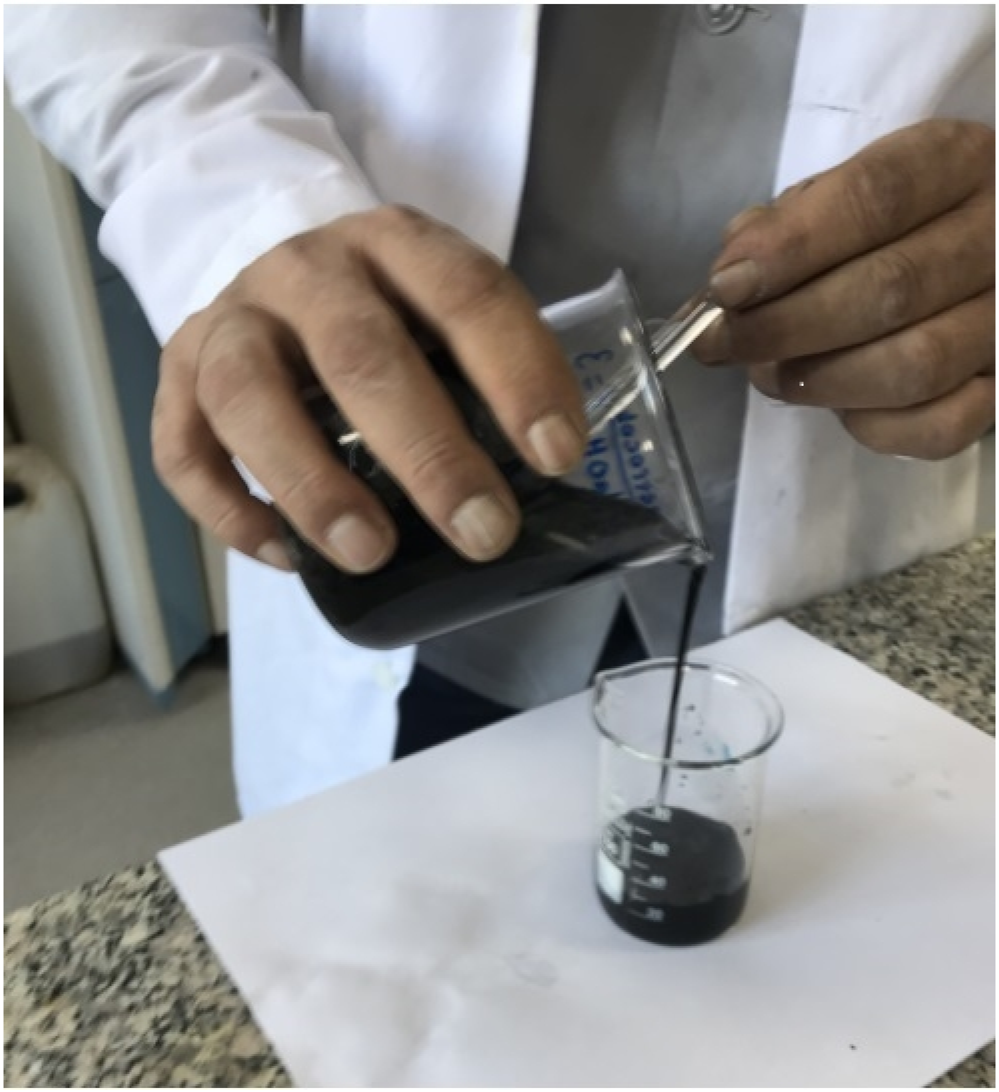

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