# The Removal of Organic Sulfur from Two Turkish Lignites by Chlorinolysis

**Yücel Y. KADIOĞLU**[*]**& Semra KARACA**

*Department of Chemistry, Atatürk University,*

*25240 Erzurum - TURKEY*

**Samih BAYRAKÇEKEN**

*Department of Chemistry, Atatürk University,*

*25240 Erzurum - TURKEY*

**M. Şahin GÜLABOĞLU**

*Department of Chemistry Engineering*

*Atatürk University, 25240 Erzurum - TURKEY*

The removal of organic sulfur from two Turkish lignites by chlorinolysis with chlorine gas in water and water-carbon tetrachloride media at ambient pressure was examined. The effects of stirring speed (5-20 s$^{-1}$), particle size (250-425, 150-180 and 74-88 $\mu$m), temperature (13-70°C) and time (0-10800 s) were investigated. Significant portions of the organic sulfur in the coal samples were removed.

## Introduction

The utilization of coals for both energy production and various coal conversion processes is limited by the presence of sulfur in the coal. The high sulfur dioxide emissions caused by the utilization of coals as a major fossil fuel leads to worldwide environmental problems.

Sulfur in coal occurs in various forms: pyrite, elemental sulfur, inorganic sulfates, minor amounts of inorganic sulphides other than pyrite, and organic sulfur[1-5]. Organic sulfur is a general classification that includes all forms of sulfur organically bound to the actual coal matrix[1,5]. The exact forms of organosulfur present in coal are unknown; however, some deductions about these forms can be made. Most information has been obtained in order to discriminate between different families of organic sulfur-containing substances using a variety of techniques and methods[4-9]. The structure of the organic radical connected to the sulfur atom has a deterministic effect on the rate of the reaction of the sulfur group.

The chemistry, thermodynamics and kinetics of the reactions of the organic sulfur groups have been reviewed[3-11]. The most important sulfur groups in coals are the following:[4,5,9-12]

1. Thiophenes, which are heteroaromatic compounds, are very stable and do not decompose thermally up to very high temperatures.

2. Aryl sulphides, in which the sulfur is connected to an aromatic ring, are usually very stable because the sulfur is adjacent to an aromatic ring and takes part in the ring resonance.

3. Aliphatic sulphides, are relatively unstable and tend to decompose to unsaturated compounds and $H_2S$.

4. Cyclic sulphides, in which the sulfur is part of nonaromatic ring, are more stable than aliphatic but less stable than aromatic sulphides.

5. Thiols (aryl and aliphatic thiols) and disulphides are unstable and tend to decompose easily to $H_2S$ and to unsaturated compounds.
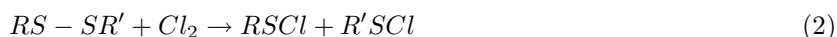
Precombustion removal of sulfur from coal can be subdivided into two types of processes, physical and chemical. Of these, physical processes can remove any soluble sulfates and most of the coarse pyrite, but microcrystalline pyrite and the organic sulfur remain largely untouched[2,13,14]. A number of chemical processes are under development with the intent to remove all of the pyrite and at least a portion of the organic sulfur. A number of chemical methods have been reviewed[14−16].

One of the most promising chemical processes is desulfurization by chlorination of coal[2,12,17−20]. Studies done on desulfurization by chlorination of coal in the gas phase at high temperature and elevated pressure have shown that both organic and inorganic sulfur can be removed to a certain extent[19,20]. The major disadvantage of chlorination directed at coal desulfurization is the use of relatively high temperatures and pressures. Strong chlorine bonding to the coal matrix leaves an unacceptably high residul chlorine content in processed coal. Another disadvantage of the process is the high loss of coal ($\sim$ 20 %) in processing[17,18].
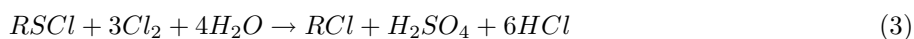
The chemical desulfurization process designated as low temperature chlorinolysis and developed at the Jet Propulsion Laboratory (JPL) in Pasedana, California, constitutes slurry-phase chlorination of coal in aqueous and organic media. This process removes both pyrite and organic sulfur (up to 60 % of organic sulfur) from coal as water-soluble sulphates under mild reaction conditions (50-100°C, atmospheric pressure)[12,18−20].

Part of the chlorine reacts with the sulfur while the rest reacts with the organic matrix. The reactions of the organic sulfur during chlorination may be summarized as follows[12,17−21]:

in an organic medium,

$$RSR' + Cl_2 \rightarrow RSCl + R'Cl \tag{1}$$

$$RS - SR' + Cl_2 \rightarrow RSCl + R'SCl \tag{2}$$

in the presence of water,

$$RSCl + 3Cl_2 + 4H_2O \rightarrow RCl + H_2SO_4 + 6HCl \tag{3}$$

where $R$ and $R'$ represent hydrocarbon groups in coal. Sulfur converted to water-soluble sulfates during chlorination is leached out by washing with water at 60°C. After hydrolysis, the coal is dechlorinated by heating at 350-550°C in steam or inert gas in accordance with the following reactions:

$$RCl + H_2O(g) \rightarrow ROH + HCl \tag{4}$$

$$R'H + RCl \rightarrow RR' + HCl \tag{5}$$

This desulfurization method offers several advantages[17]: a high degree of sulfur can be removed, particularly organic sulfur; the process can be conducted at low temperatures and atmospheric pressure;

the reagent used, chlorine, is regenerable by the conversion of HCl recovered from the above three stages to chlorine.

Relatively few studies have been done on the removal of organic sulfur from coal by chlorination. In the present study, the removal of organic sulfur from two Turkish lignites by chlorination was investigated. The effects of chlorination time, particle size, temperature, stirring speed and water-carbon tetrachloride ratio were studied in water and water-carbon tetrachloride media.

# Experimental

## Materials

The coal samples used in this investigation were collected from the Dadağı and Mengen coal mines in Turkey. The samples were air dried, ground and then sieved to give 250-425, 150-180 and 74-88 $\mu$m size fractions using ASTM standard sieves. The average results of duplicate analyses performed according to ASTM procedures for the two coal samples are given in Table 1.

**Table 1.** Proximate sulfur form analysis and heating value of studied coals. Results are averages of duplicate analyses (as received)

|  | Coal | |
| --- | --- | --- |
|  | Dadağı | Mengen |
| Proximate analyses (wt %) | | |
| Ash | 21.05 | 25.93 |
| Volatile matter | 35.98 | 41.58 |
| Fixed carbon | 37.04 | 26.21 |
| Moisture | 5.93 | 6.28 |
|  | | |
| Sulfur distribution (wt %) | | |
| Total | 7.93 | 12.25 |
| Sulfate | 0.25 | 0.06 |
| Pyritic | 4.31 | 1.69 |
| Organic | 3.37 | 10.50 |
| Heating value (cal/g) | 5936 | 5825 |

## Methods

The chlorination experiments were carried out in a 250 ml glass flask reactor immersed in a thermostatically-controlled water bath at ambient pressure ($\cong$ 610 mm Hg) and furnished with a mechanical stirrer, a chlorine gas bubbler and a reflux condenser. For each run, 6g of coal plus 150 ml of water or water-carbon tetrachloride (5 ml water + 145 ml carbon tetrachloride for Dadağı coal and 10 ml water + 140 ml carbon tetrachloride for Mengen coal) presaturated with chlorine gas at the desired temperature were placed in the reactor and heated to the desired temperature while maintaining the agitator speed at 14 s$^{-1}$ and chlorine gas was then bubled through the suspension for various periods of time. In the experiments, the gas flow rate was kept constant at 350 ml min$^{-1}$, unless otherwise stated.

Following the treatment in aqueous media, the reactor contents were rapidly filtered and washed with distilled water. The solid was then dried in an oven for 2h at 105 $^\circ$C, cooled and weighed. The organic sulfur

content was determined[22,23] and analyzed by Eschka's method.

In the water-carbon tetrachloride runs, the solvent phase was evaporated following chlorination under reduced pressure and then 350 ml of distilled water was added to the chlorinated coal. The coal was hydrolyzed at the boiling temperature ($94\,^\circ$C) of water for two hours, filtered and washed with distilled water. The coal filter cake was dried in an oven for 2h at $105\,^\circ$C, cooled and weighed. The organic sulfur content was determined as stated before[22,23].

# Results and Discussion

## Effect of Stirring Speed

In order to study the effect of stirring speed on the removal rate of organic sulfur, both Dadağı and Mengen coal samples in water and water-carbon tetrachloride media were chlorinated at controlled speeds between 5 to 20 s$^{-1}$ at $40\,^\circ$C. The results are shown in Fig. 1,a-d.



**(a)**
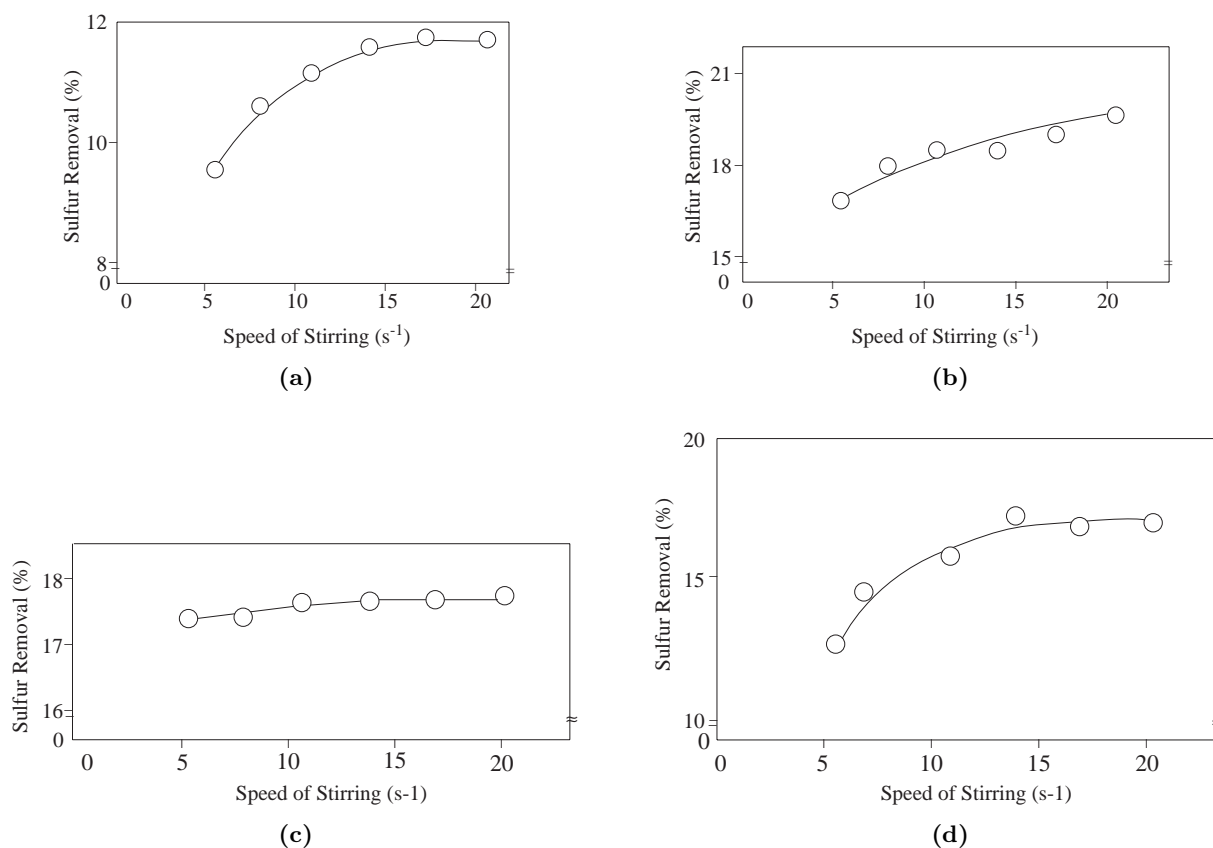
**(b)**

**(c)**

**(d)**

**Figure 1.** Effect of stirring speed on the removal rate of organic sulfur in water medium [ Dadağı coal (A), Mengen coal (B)] and water-carbon tetrachloride medium [ Dadağı coal (C), Mengen coal (D)]. Particle size = 250-425 $\mu$m; time = 3600 s; temperature = $40\,^\circ$C; gas flow rate = 350 ml min$^{-1}$; solid-to-liquid = 1/25.

In both media, the rate of organic sulfur removal increased slightly with the increase in speed of rotation up to 14 s$^{-1}$. From this it may be concluded that dissolution is a physically-controlled process, because in general the rate of physical processes is considerably more sensitive to changes in stirring speed

than is the rate of chemical processes. The reaction may be largely controlled by either the diffusion of chlorine through the fluid film surrounding the solid particle, or the diffusion of the product species away from the particle surface[24,25].

Any further increase in stirring speed had little or no effect on the rate of organic sulfur removal. Therefore, a speed of 14 s$^{-1}$ was used for the rest of the experiments.

## Effect of Particle Size

Experiments were conducted to investigate the effect of particle size on organic sulfur removal from Dadağı and Mengen coals in water and water-carbon tetrachloride media at 40°C at three particle sizes (250-425, 150-180 and 74-88 $\mu$m). The results are shown in Fig. 2, a-d.
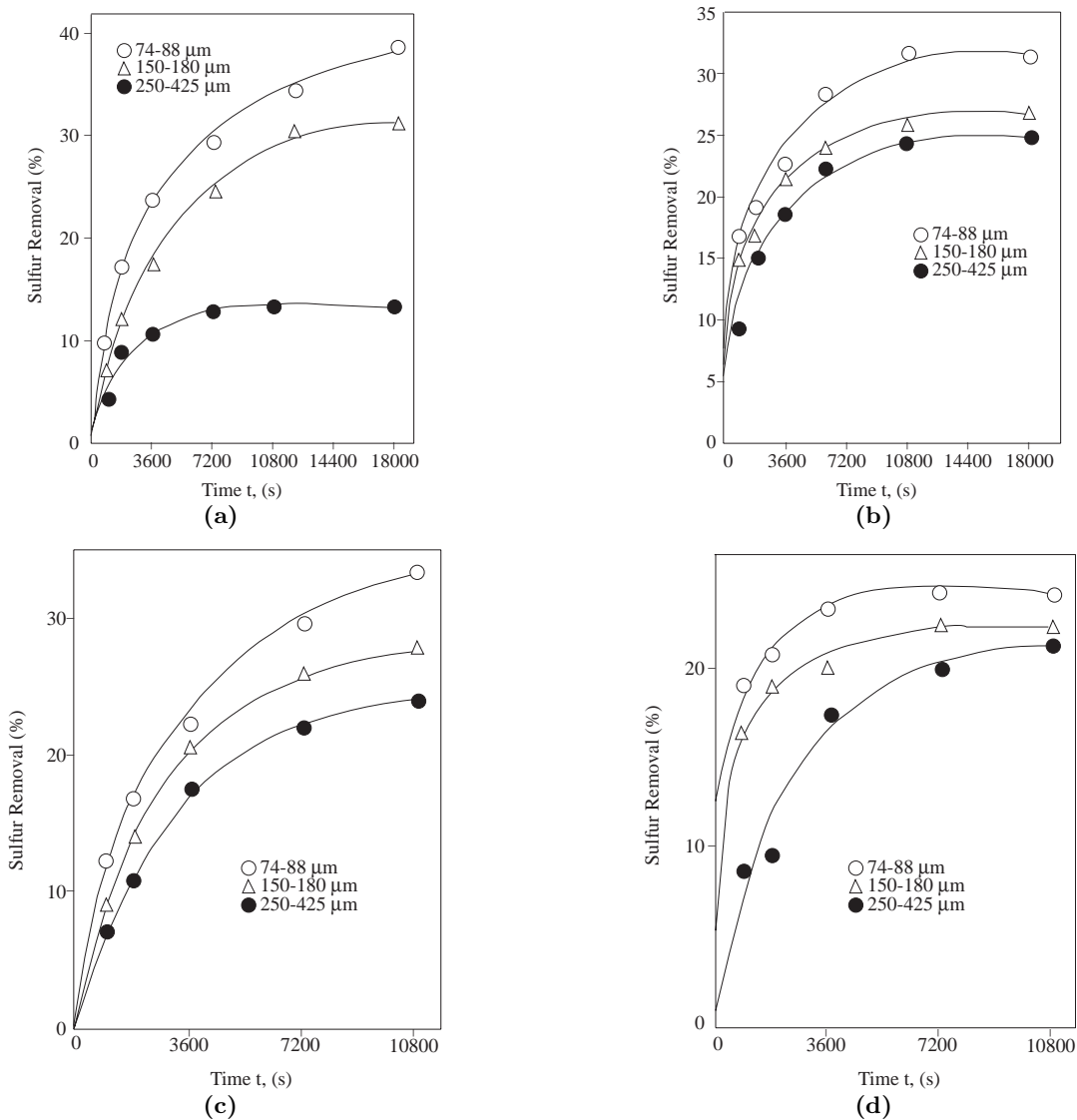


**Figure 2.** Effect of particle size on the removal rate of organic sulfur in water medium [ Dadağı coal (A), Mengen coal (B)] and water-carbon tetrachloride medium [ Dadağı coal (C), Mengen coal (D)]. Temperature = 40°C; gas flow rate = 350 ml min$^{-1}$; stirring speed = 14 s$^{-1}$; solid-to-liquid = 1/25.

As can be seen in these figures, the rate of removal of organic sulfur in both media for both coals increased with decreasing particle size, implying a surface reaction. Decrease in coal particle size results in an increase in external surface area. An increase in surface area would lead to an increase in the surface reaction rate[24].

It was found that at 74-88 $\mu$m particle size, at 40°C, a treatment time of 180 min was sufficient to maximize the removal of organic sulfur by this process.

In both media, the total reduction in organic sulfur was much lower with Mengen coal than with Dadağı coal under the same reaction conditions. This may be accounted for by differences in rank and differences in the concentration of labile organic sulfur functional groups[4,10,18,21].
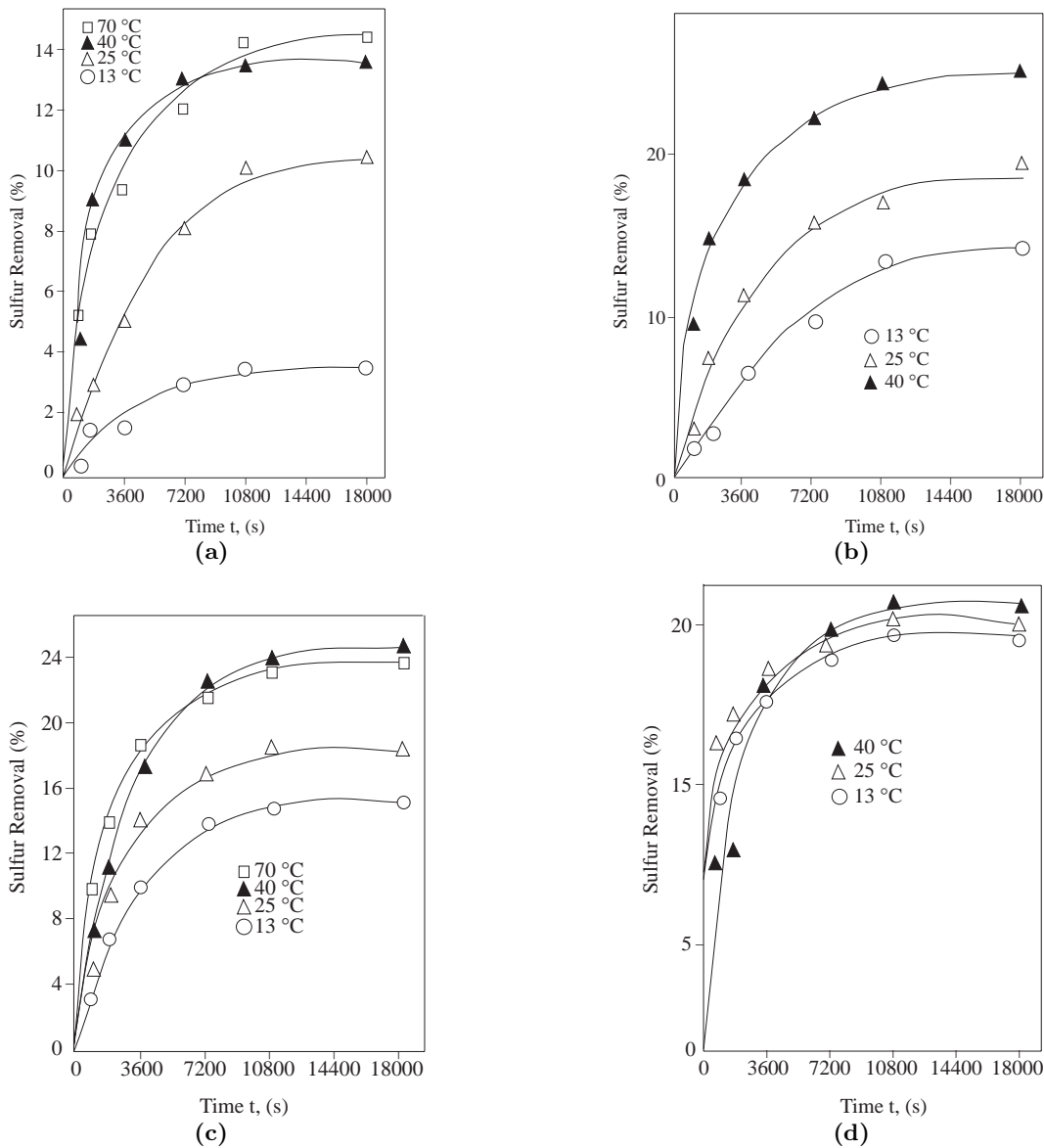


**Figure 3.** Effect of temperature on the removal rate of organic sulfur in water medium [ Dadağı coal (A), Mengen coal (B)] and water-carbon tetrachloride medium [ Dadağı coal (C), Mengen coal (D)]. Particle size = 250-425 $\mu$m; gas flow rate = 350 ml min$^{-1}$; stirring speed = 14 s$^{-1}$; solid-to-liquid = 1/25.

## Effect of Temperature

The effect of temperature on organic sulfur removal from Dadağı and Mengen coals was studied in both water and water-carbon tetrachloride media. The degree of organic sulfur removal as a function of reaction time for temperatures between 13-70°C is illustrated in Fig.3, a-d. As seen in these figures, the reduction of organic sulfur increases with increasing temperature, but changes in temperature between 40°C and 70°C appear to have little effect on the rate. This may be explained by considering such competing effects as an increase in the reaction rate and a decrease in the chlorine solubility with increasing temperature[18,26]. However, the removal rate of organic sulfur under similar reaction conditions was influenced by increase in temperature more significantly in the water medium then in the water-carbon tetrachloride medium.

In the water medium, the chlorination of Mengen coal produced a significant reduction ($\sim$ 26.0 % at 40°C) in organic sulfur while chlorination of Dadağı coal had only a slight reduction ($\sim$ 13.0 % at 40°C). This may be attributed to differences of the thermodynamics and the kinetics of the reactions with chlorine of the various organic sulfur groups present in the coals[12,18]. For example, it has been shown[18] that thiophenic sulfur in coal cannot be removed under mild conditions of chlorinolysis.

## Effect of Water-to-Carbon Tetrachloride Ratio

The effect of the water-to-carbon tetrachloride ratio on the removal rate of organic sulfur was investigated for both coal samples. For this purpose, a series of tests were conducted at 25°C with varied ratios of water-to-carbon tetrachloride. As seen in Fig. 4, a-b, the reduction of organic sulfur increased with increasing water amount in the water-carbon tetrachloride mixture up to a certain water-carbon tetrachloride (67 %) ratio, after which it began to decrease. According to these data, the products formed during the reaction of organic sulfur in coal with chlorine might be said to dissolve with an increasing of water, thus exposing fresh surface sites for reaction[17,27]. But beyond a certain water-to-carbon tetrachloride (67 %) ratio, the decrease of the dissolution rate of organic sulfur may be due to a decrease in the solubility of chlorine with the increasing water ratio[27].
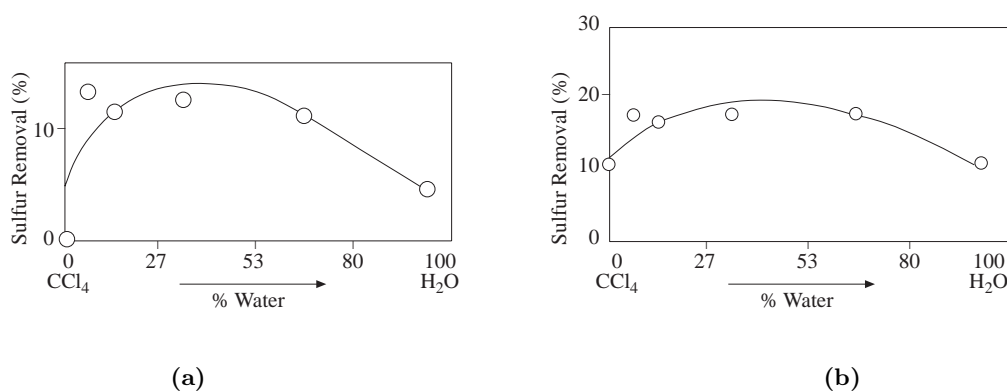


(a)                                                        (b)

**Figure 4.** Effect of water-to-carbon tetrachloride ratio on the removal rate of organic sulfur [ Dadağı coal (A) and Mengen coal (B)] Particle size = 250-425 $\mu$m; time = 3600 s; temperature = 25°C; stirring speed = 14 s$^{-1}$; gas flow rate = 350 ml min$^{-1}$; s solid-to-liquid = 1/25.

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