

Adsorptive Desulfurization of JP-8 Fuel Using Ag^+ /Silica Based Adsorbents at Room Temperature

by Dat T. Tran, Zachary W. Dunbar, and Deryn Chu

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Sensors and Electron Devices Directorate, ARL

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14. ABSTRACT We report an adsorptive desulfurization of Army JP-8 fuel using silver ions (Ag ⁺) tethered to porous silica at ambient conditions. Mesoporous silica—both one- and two-dimensional MCM-41 and MSUH, respectively—were studied as adsorbent support materials for the desulfurization of liquid phase JP-8 fuel. In this work, silver loadings up to ~33 wt.% on silica support materials were prepared and evaluated for the adsorptive desulfurization of JP-8 jet fuel. These adsorbents were characterized using JP-8 fuel containing ~400 ppmw sulfur at room temperature. The sulfur adsorption capacities of Ag ⁺ (31.8 wt.%)/MSUH and Ag ⁺ (32.8 wt.%)/MCM-41 with static adsorption experiments were 24.0 and 26.4 mgS/g adsorbent, respectively. The sulfur adsorption capacities of Ag ⁺ (31.8 wt.%)/MSUH, Ag ⁺ (32.8 wt.%)/MCM-41, and Ag ⁺ (28.1 wt.%)/MSUH+MCM-41 with packed-bed adsorption experiments were 40.0, 31.8, and 24.3 mgS/g adsorbent, respectively. Sulfur removal and adsorption characteristics for these sorbents are described.					
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1. Introduction

The growth demand for alternative power generation from JP-8 fuel is a pinnacle focus area of the U.S. Army's fuel processing research and development efforts. The primary challenge in fuel processing of JP-8 to produce fuel-cell-quality hydrogen is liquid phase desulfurization (figure 1). Any organic sulfur compounds in the fuel are converted into hydrogen sulfide in the fuel processing reformer, resulting in poisoning the reformation catalysts as well as poisoning downstream operations. Therefore, it is essential to remove these undesired organic sulfur compounds in the liquid phase before they access the reformer. While gas phase sulfur removal technologies exist, these systems tend to be massive and process the fuel stream post-reformation. Sorbents for the processing of liquid fuel JP-8 are not as developed as gas phase sorbents, but must still meet the challenging design criteria of reducing sulfur levels to 1 ppmw or less in order to protect the reformation catalysts from potential poisoning (1).

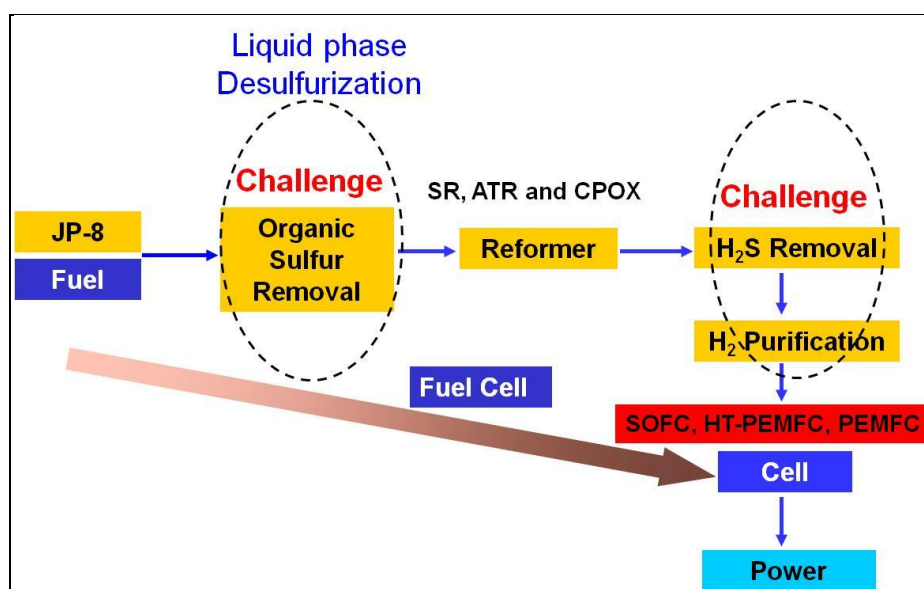


Figure 1. Schematic diagram of logistic fuel processing.

Adsorbents with a high capacity for desulfurization of liquid fuels have garnered interest in the literature. Many different sorbents have recently been developed for removing organic sulfur compounds from the fuels, such as gasoline, diesel, jet fuels, and/or model fuels. Adsorptive desulfurization approach is highly promising because it is accomplished at ambient temperature and pressure. Erkey and co-workers used carbon aerogels (CAs) as adsorbents for their sulfur removal studies from a model fuel. They found that CAs with larger average pore size yielded a high sulfur adsorption rate and a high capacity for dibenzothiophene (DBT) (2, 3). McKinley and Angelici reported their investigation using silver ion (Ag^+)/SBA-15 and Ag^+ /silicon dioxide (SiO_2) as sorbents with various loadings of silver tetrafluoroborate (AgBF_4) up to 45 wt.% for

selective adsorption of DBT and 4,6-dimethyldibenzothiophene (DMDBT), reducing from an initial sulfur concentration of 411 ppm to the final sulfur concentrations of 8 and 13 ppm, respectively (4). Yang et al. showed that their study on adsorption of thiophene with the highest capacity of 2.8 mgS/g adsorbent using a xerogel-derived zinc (Zn)-based nanocrystalline aluminum oxide, Zn (20 wt. %)/aluminum oxide (Al_2O_3) (5). Cychosz et al. used the metal-organic framework known as microporous coordination polymers (MCP) to remove organosulfur compounds in liquid phase, such benzothiophene (BT), DBT, and DMDBT (6).

Other works have reported their development of adsorptive desulfurization using ion exchange zeolite- and nickel (Ni)-based adsorbents (7–9). The adsorptive desulfurization of fractionated light JP-8 (380 from 736 ppmw) over the Ni/ SiO_2 - Al_2O_3 adsorbent were found to have a high sulfur adsorption capacity of about 11.5 mgS/g adsorbent. Wang and Yang reported the desulfurization of a model jet fuel by adsorption method using carbon-based sorbents (10). Nair and Tatarchuk found that Ag/titanium oxide (TiO_2) sorbents removed sulfur from JP-5 fuel containing 1172 ppmw and JP-8 fuel containing 630 ppm (11, 12). This sorbent with Ag (4 wt. %)/ TiO_2 demonstrated a saturation sulfur capacity of 6.3 mgS/g for JP-5 and 2.9 mgS/g for JP-8 at ambient conditions. Such other studies rather than adsorptive desulfurization method also reported in the literature, these approaches are oxidative desulfurization of organosulfur compounds (13–15), electrochemical catalytic oxidation (16), and sulfur removal of model fuel via a combination of catalytic oxidation and extraction in ionic liquid (17).

Hydrogen production through fuel reformation for fuel cell applications has been studied by several methods such as steam reforming (SR), auto-thermal reforming (ATR), and catalytic partial oxidation reforming (CPOX) (18–23). Logistic fuel desulfurization processes reduce the burden for reformer and fuel cell catalysts due to sulfur poisoning. In this report, we describe the preparation of silver on mesoporous silica support as sorbents for organic sulfur removal from liquid phase JP-8 fuel at ambient conditions, using adsorptive desulfurization approach.

2. Experimental Section

2.1 Materials

All chemicals were purchased from Sigma-Aldrich and used as received (silver nitrate [AgNO_3], $\geq 99\%$; silica, mesostructured, MCM-41, hexagonal, pore size: 2.3–2.7 nm, Brunauer, Emmett and Teller theory [BET] surface area: $\sim 1000 \text{ m}^2/\text{g}$; and silica, mesostructured, MSUH, large pore two-dimensional [2-D] hexagonal, pore size: 7.1 nm, BET surface area: $\sim 750 \text{ m}^2/\text{g}$). JP-8 fuel was obtained from Fort Belvoir, VA, and had a sulfur concentration of ~ 400 ppmw.

2.2 Preparation of Ag Ions on Silica Particles

All samples (Ag^+/MSUH , $\text{Ag}^+/\text{MCM-41}$, and $\text{Ag}^+/\text{MSUH} + \text{MCM-41}$) were prepared in the same manner as an aqueous wet impregnation method to load the silver. Typically, 0.5 g of silica was placed in a 100 mL glass beaker, followed by an addition of 3 mL of aqueous solution containing 0.5 g of AgNO_3 in a dropwise manner. The solution was shaken by a shaker gently for several hours, after that it was dried in a vacuum oven at 40 °C, and then transferred to another vacuum oven at 110 °C in a dry room (~0% humidity) before use. The silver loading was determined to be ~32 wt.% on MSUH silica, 32.8 wt.% on MCM-41 silica, and 28.1 wt.% on MSUH+MCM-41, as measured by inductively coupled plasma – mass spectrometry (ICP-MS).

2.3 Materials Characterization

The morphology of the silica and coated materials were examined using a scanning electron microscope (SEM) (FEI QUANTA 200 F) at an accelerating voltage of 20 kV. The samples were sputter-coated to reduce charging before SEM operation. BET surface areas of the samples were additionally measured by Micromeritics TriStar II (TriStar II 3020 V1.03) using N_2 gas as adsorptive for physisorption at 77.3 K. Adsorption/desorption isotherm measurements were collected in the relative pressure range P/P_0 from 0.01 to 1.00. The samples were pre-treated in an oven at 40 °C under vacuum overnight and then de-gassed at 110 °C prior to the adsorption analysis. ICP-MS (PerkinElmer ELAN® ICP-MS) was used to confirm the weight percentage of silver in the adsorbent samples. Prior to analysis, $^{107}\text{Ag}^+$ detection with the spectrometer was standardized with solutions made by diluting a 10 mg/L atomic absorption standard solution (PerkinElmer Pure Plus) with deionized water to 0.1, 1, and 2.5 ppmw.

2.4 Static Adsorption Experiments

Sulfur removal from real JP-8 fuel was carried out in a static reactor using a 100-mL beaker under static condition without stirring at room temperature, 20 °C. Typically, four reactions were examined at the same time with two served as blanks and the other two as real adsorbents. Each sample containing 0.050 g of adsorbent of MCM-41 (blank), MUSH (blank), $\text{Ag}^+/\text{MCM-41}$, Ag^+/MSUH , and 5 g JP-8 fuel were placed in a beaker for sulfur removal test. The reactions were stopped after two days for sulfur analysis.

2.5 Packed-bed Adsorption Experiments

The following conditions were used as reported in our recent study using Au^+/SiO_2 as adsorbent (24). Pretreatment of the adsorbents were conducted by heating under vacuum to 110 °C overnight to remove any gas or trapped water. The prepared materials were then packed in a 4.6 mm ID (internal diameter) and 50 mm length column (Chromtech) inside a 0% humidity dry room. JP-8 fuel containing an initial sulfur concentration of ~400 ppmw was pumped into the column using a Shamatzu HPLC pump. The liquid fuel flow rate was operated at 0.25 mL/min.

The liquid hourly space velocity (LHSV) was 18. Test conditions for the packed column reactor were as follows:

- Ag⁺/MSUH: 20 °C, 233.6 mg adsorbent of Ag⁺(31.8 wt.%)/SiO₂
- Ag⁺/MCM-41: 20 °C, 334.3 mg adsorbent of Ag⁺(32.8 wt.%)/SiO₂
- Ag⁺/MSUH+MCM-41: 20 °C, 403.8 mg adsorbent of Ag⁺(28.1 wt.%)/SiO₂
- Pressure drop: All samples packed in the column demonstrated a 0.1 to 2 MPa pressure drop at the above conditions.

Sample effluent was collected from the packed-bed column in 1-mL aliquots, which were subsequently analyzed for total sulfur concentration using a ultraviolet (UV) total sulfur analyzer (multi EA 3100, Analytikjena) with the detection limit less than 0.5 ppm. Sulfur removal of real JP-8 fuel is expressed by the equation:

$$X_{\text{sulfur}} = ([S]_{\text{initial}} - [S]_{\text{final}}) / [S]_{\text{initial}} \times 100\%. \quad (1)$$

Using the data from the total sulfur analysis, it was then possible to determine the sulfur capacity of the adsorbent by integrating under the curve of the sulfur removal data and normalizing per unit mass.

The major organic sulfur compounds in JP-8 fuel have previously been analyzed in our laboratory and described earlier (25).

3. Results and Discussion

3.1 Preparation and Morphology of Adsorbents

Both pure silica can be seen in figure 2a and 2b. The scale bar is 1 μm. ICP-MS showed that weight percentages of silver in Ag⁺/MSUH, Ag⁺/MCM-41, and Ag⁺/MSUH+MCM-41 are to be 31.8, 32.8, and 28.1 wt.%, respectively.

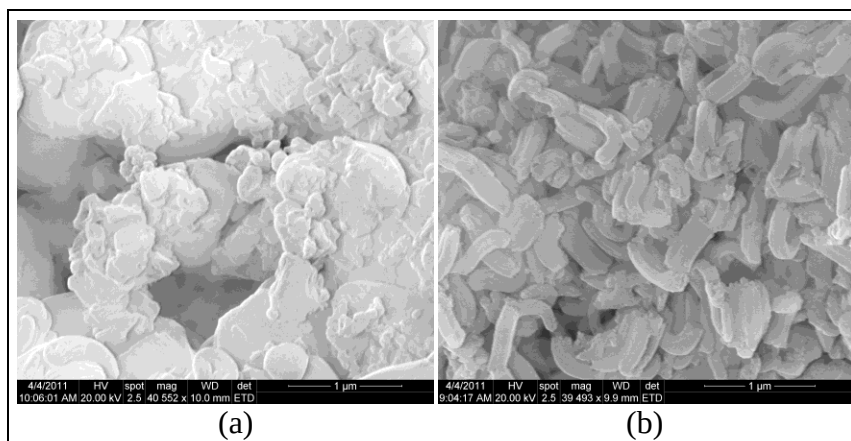


Figure 2. SEM micrographs of (a) 1-D mesoporous silica powder, MCM-41, and (b) 2-D mesoporous silica powder, MSUH.

Table 1 summarizes the BET surface areas of adsorbents before and after loading silver on silica, and weight percentages of silver on each adsorbent.

Table 1. Surface area (m^2/g) & Ag analysis of sorbents measured by BET and ICP-MS.

Sample	Without Ag	With Ag	Ag (Wt.%)
MSUH (2-D)	727.7	207.3	31.8
MCM-41 (1-D)	843.4	341.9	32.8
MSUH+MCM-41	-----	202.4	28.1

3.2 Adsorption Characteristics of Adsorbents

In this study, Ag ions coated on silica particles (Ag^+/MSUH , $\text{Ag}^+/\text{MCM-41}$, and $\text{Ag}^+/\text{MSUH+MCM-41}$) were used as adsorbents, respectively. While many reports in the literature restrict their analyses to model fuels (e.g., iso-octane or hexadecane) at moderate temperature and/or containing a single known sulfur compound (e.g., thiophene, benzothiophene or dibenzothiophene) (4, 14–15, 26), just to mention a few. Our approach for evaluating these adsorbents was to test their capability to directly remove organosulfur compounds in a real JP-8 fuel at ambient conditions. This method used an actual JP-8 fuel.

Static adsorption experiments were performed in a beaker under static condition without stirring at ambient conditions. Figure 3 shows the results of desulfurization capacity of JP-8 fuel after two days with pure silica versus silver ions loading on silica. The pure silica showed a poor adsorption of organosulfur compounds, 1.29 mgS/g MSUH and 1.38 mgS/g MCM-41, while adsorbents with silver coated on silica demonstrated a significantly high amount of sulfur affinity, 24.0 mgS/g Ag^+ (31.8 wt.)/MSUH and 26.4 mgS/g Ag^+ (32.8 wt.)/MCM-41. This high increase in sulfur removal capacity is attributed to the amount of silver loading on silica, which can be seen in another report (4).

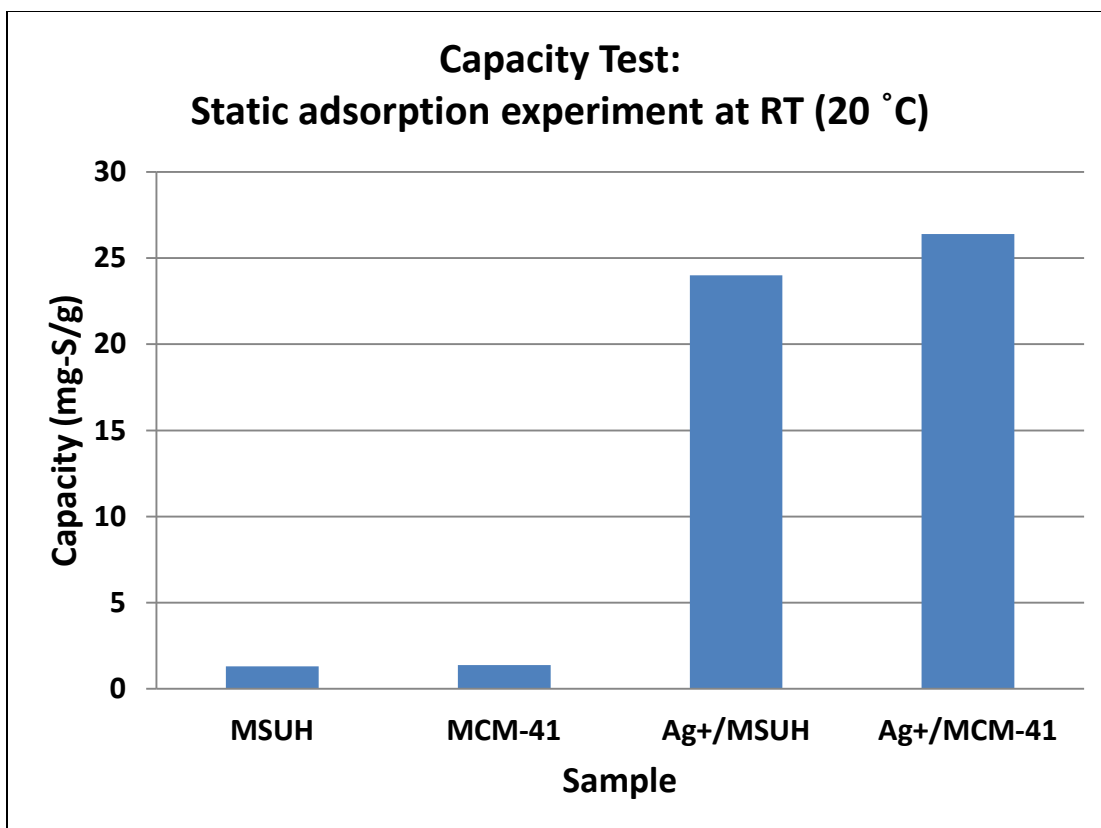


Figure 3. Desulfurization capacity of JP-8 fuel under static adsorption conditions without stirring after two days at room temperature (20 °C).

Packed-bed adsorption experiments were carried out in a column reactor at room temperature, using a liquid pump to pump the JP-8 fuel through the reactor. Treated fuels were collected for sulfur analysis. Figure 4 shows the result of sulfur adsorption of Ag⁺ coated on mesoporous MSUH silica particles, Ag⁺(31.8 wt.%)/MSUH. The initial performance of sulfur removal from JP-8 fuel is nearly 100% but gradually drops down and plateaus at around 68%–70% sulfur removal before dropping below 50% after 40 mL of JP-8 fuel processed. The results of total sulfur analysis allow determination of the sulfur adsorption capacity by integrating under the curve and normalizing per unit mass. This adsorbent demonstrated a sulfur adsorption capacity of 40.0 mgS/g adsorbent, which is very high as compared to others in literature.

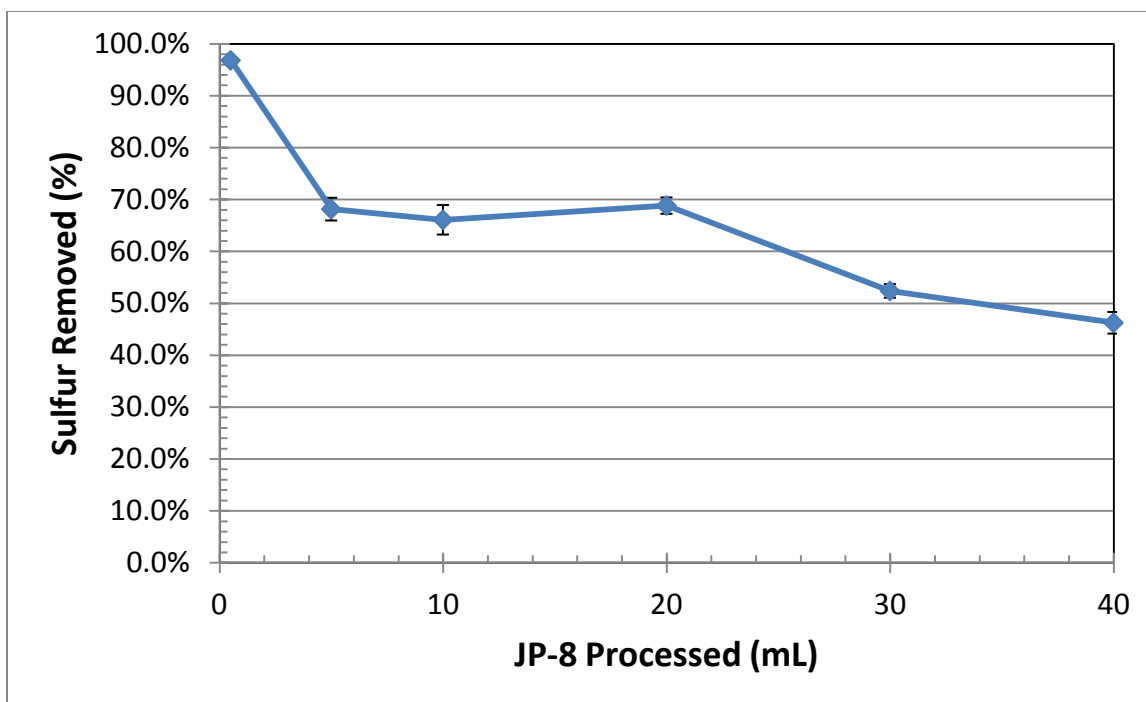


Figure 4. JP-8 fuel desulfurization at room temperature of Ag^+ (31.8 wt.)/MSUH adsorbent. The error bars on the adsorption data represent corrected standard deviation of repeated measurements for each aliquot.

Figure 5 reveals the result of sulfur adsorption of Ag^+ coated on mesoporous MCM-41 silica particles, Ag^+ (32.8 wt.)/MCM-41. The initial desulfurization of JP-8 fuel is nearly 100% but slowly drops down and stays plateau at around 70% sulfur removal before dropping below 50% after 40 mL of JP-8 fuel processed. This adsorbent demonstrated a sulfur adsorption capacity of 31.8 mgS/g adsorbent upon integrating under the curve and normalizing per unit mass.

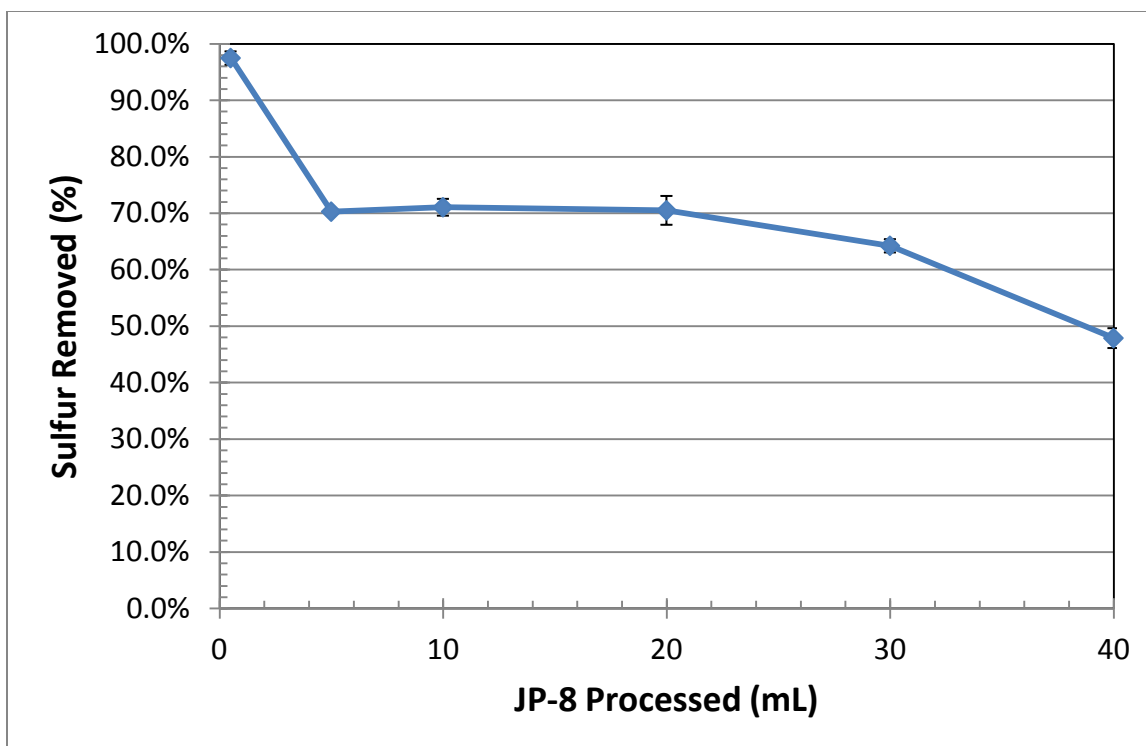


Figure 5. JP-8 fuel desulfurization at room temperature of Ag^+ (32.8 wt.%) / MCM-41 adsorbent. The error bars on the adsorption data represent corrected standard deviation of repeated measurements for each aliquot.

The use of one-dimensional (1-D) and 2-D mesoporous silica above as supporting materials for silver ions loading proves that these adsorbents worked quite well for desulfurization of real JP-8 fuel. In addition to the above adsorbents, we combined both 1-D and 2-D mesoporous silica together as a supporting material. In the same manner, we loaded the silver ions on this supporting material and used it as an adsorbent, Ag^+ (28.1 wt.%) / MUSH+MCM-41, for sulfur removal from JP-8 fuel. Figure 6 shows the initial desulfurization of JP-8 fuel is nearly 100% but slowly drops down and stays plateau at around 65% sulfur removal before dropping below 55% after 40 mL of JP-8 fuel processed. This adsorbent demonstrated a sulfur adsorption capacity of 24.3 mgS/g adsorbent upon integrating under the curve and normalizing per unit mass.

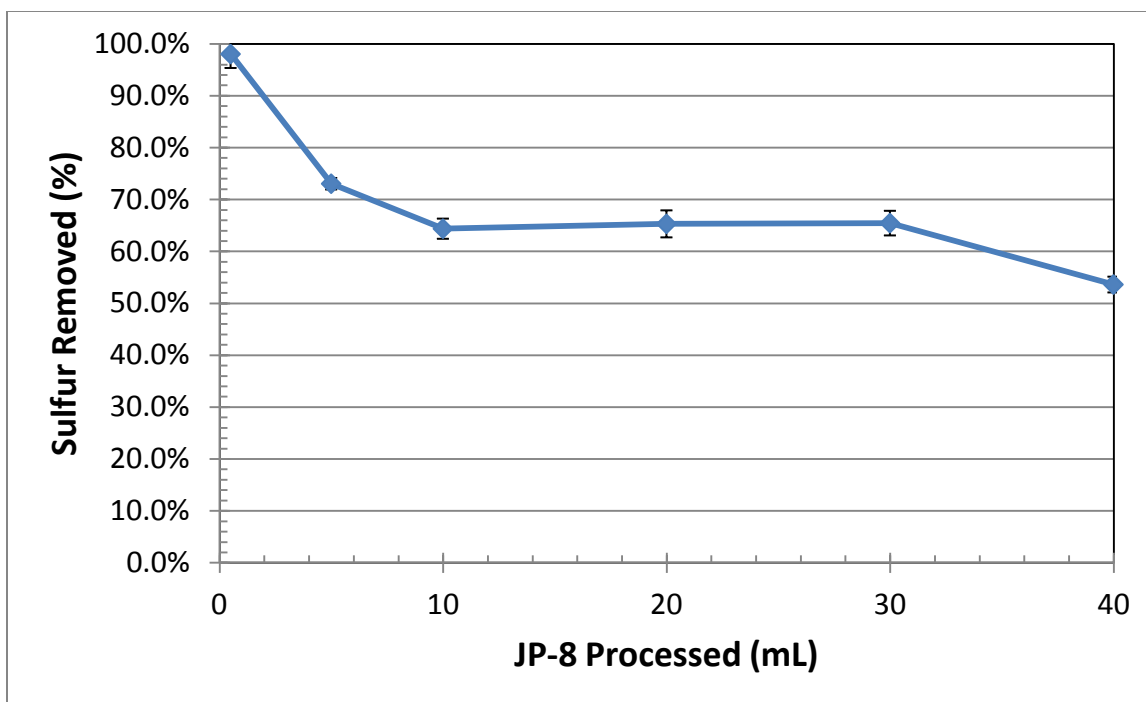


Figure 6. JP-8 fuel desulfurization at room temperature of Ag^+ (28.1 wt. %)/MSUH+MCM-41 adsorbent. The error bars on the adsorption data represent corrected standard deviation of repeated measurements for each aliquot.

We observed that sulfur adsorption under ambient conditions by packed-bed column experiments show higher desulfurization capacity compared to static adsorption experiments. This phenomenon is attributed to pressure built up in the packed-bed column. The liquid pump provides a pressure of up to 2 MPa to pump through the tightly packed column, which may be sufficient pressure to force fuel deeper into the pore network of the silica support, relative to the static tests which lack this additional driving force.

To restore adsorptive performance to these adsorbents, pure iso-octane was pumped through the reactor column. This regeneration process caused adsorbed organic sulfur compounds to desorb and diffuse into the clean iso-octane stream. The result of this regeneration approach, however, did not restore to 100% original adsorption capacity (data not shown).

4. Conclusions

Liquid phase desulfurization of JP-8 fuel is a crucial technology for reducing the poisoning of the reformers' and fuel cells' catalysts. This work demonstrated a high capacity sulfur sorbent using 1- and 2-D mesoporous silica as supporting materials for silver ions, with silver loading up to ~33 wt.%. For static adsorption experiments, the desulfurization capacities of real JP-8 fuel were found to be 24.0 and 26.4 mgS/g adsorbent for Ag^+ (31.8 wt.+)/MSUH and Ag^+ (32.8 wt.+)/MCM-41, respectively. The sulfur adsorption capacities of Ag^+ (31.8 wt.+)/MSUH, Ag^+ (32.8 wt.+)/MCM-41, and Ag^+ (28.1 wt.+)/MSUH+MCM-41 with packed-bed adsorption experiments were 40.0, 31.8, and 24.3 mgS/g adsorbent, respectively. An attempt to regenerate the adsorbent was not successful. Research is underway to improve the regenerability. We are continuing to develop this technology in order to facilitate hydrogen generation for the Army of the future.

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List of Symbols, Abbreviations, and Acronyms

1-D	one-dimensional
2-D	two-dimensional
Ag ⁺	silver ion
AgBF ₄	silver tetrafluoroborate
AgNO ₃	silver nitrate
Al ₂ O ₃	aluminum oxide
ATR	auto-thermal reforming
BET	Brunauer, Emmett and Teller theory
BT	benzothiophene
CAs	carbon aerogels
CPOX	catalytic partial oxidation reforming
DBT	dibenzothiophene
DMDBT	4,6-dimethyldibenzothiophene
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
LHSV	liquid hourly space velocity
MCP	microporous coordination polymers
Ni	nickel
SEM	scanning electron microscope
SiO ₂	silicon dioxide
SR	steam reforming
TiO ₂	titanium oxide
UV	ultraviolet
Zn	zinc

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