Desulfurization of Light Diesel Fuel Using Chloramine T and Polymer Supported Imidation Agent

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Abstract

The main objective of the present work focuses on a novel desulfurization process for light diesel fuel based on the chemical adsorption of sulfur compounds on a polymer-supported imidation agent (Sodium N-chloro-polystyrene sulfonamide, PI) at ambient conditions. The activity of the synthesized PI was investigated at first with respect to the removal of DBT from model light oil (n-tetradecane containing DBT 11 (mmol/ℓ) corresponding to 500 ppm sulfur content) The present process was found to be also effective for the desulfurization of actual light diesel oil the sulfur concentration was decreased from 1900 ppm to about 180 ppm (deep desulfurization level). The effects of initial sulfur concentration in commercial oil and the sorbent dose at time equal to 40 hr on the desulfurization efficiency were studied. The results indicate that the removal efficiency increased with decreasing sulfur concentration and increasing sorbent dose. Empirical correlations for the estimation of residual sulfur in light diesel and the percentage removal efficiency in terms of the major operating parameters were proposed with 95% confidence level.

Keywords: Desulfurization, Light diesel fuel, Adsorption, Polymer, Imides

نزع الكبريت من وقود الديزل الخفيف باستخدام كلور امين-T ومادة ممتزة بوليميرية محملة بالاميدات

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الخلاصة

تضمن البحث دراسه تجريبيه لعمليه نزع الكبريت من وقود الديزل تستند على الامتزاز الكيميائي لمركبات الكبريت على سطح عامل مساعد بوليمري محمل بالأميدات (sodium N-chloro-polystyrenesulfonamide, PI) وتحت ظروف اعتياديه من درجات حراره وضغط. فعالية العامل المساعد المحضر قد تم دراستها اولا لنموذج نفطي (model light oil) هو (n-tetradecane الحاوي على $DBT\ 11\ mmol/\ell$ يقابل 500ppm محتوى كبريت). الدراسه اثبتت ايضا فعاليه هذه العمليه عند معالجة مشتق نفطي حقيقي (وقود ديزل ناتج من وحدة التكسير الهيدروجيني لمصفى بيجي الحاوي على تركيز للكبريت 1900 ppm) حيث انخفض تركيز الكبريت الى حوالي (180 ppm). تاثير التركيز الأبتدائي للكبريت في المشتق النفطي وكميه الماده الممتزه على كفاءه ازالة الكبريت قد تم دراستها حيث اشارت النتائج ان كفاءة الأزاله تزداد مع نقصان التركيز للكبريت في المشتق النفطي وزيادة كميه الماده الممتزه. تم اقتراح علاقه رياضيه تبين العلاقة بين كفاءة الأزاله للكبريت مع التركيز الأبتدائي للكبريت و كميه الماده الممتزه.

الكلمات الدالة: نزع الكبريت، وقود الديزل الخفيف، الأمتزاز، بوليمرات، أميدات

1. *Introduction:-*

Much attention has been focused on the deep desulfurization of light oil, since the sulfur oxy-acids (SOx) contained in fuel exhaust gas cause air pollution and acid rain[1]. As a result of environmental impact, strict requirements on low sulfur content in fuels are becoming prominent throughout the world. It is expected that diesel sulfur content reachs below 15 ppm in the United States, Canada and the European Union [2].

Ma et al.[3] reported obtaining ultra-low sulfur (<1 ppm) gasoline, diesel and jet fuel by adsorption on a transition metal supported on silica gel. Results showed little octane penalty from adsorption, representing an important benefit over hydrodesulfurization.

Yang et al. [4] studied the desulfurization of a commercial diesel fuel (297.2 ppm) by different nickel (II)-exchanged faujasite zeolites in a fixed-bed adsorber operated at ambient conditions. The zeolites were prepared by both liquid-phase (LP) and solid-state (SS) ion-exchange (IE) methods. The sorbents were fully regenerated in one step using air at 350 °C, which simplifies possible implementation for many applications. GC-FPD results showed that the π-complexation sorbents selectively removed highly substituted thiophenes, benzothiophenes, and dibenzothiophenes from diesel, which is not possible using conventional hydrodesulfurization (HDS) reactors or direct sulfur-metal interaction-based zeolites such as Ce(IV)-Y. The high sulfur selectivity and high sulfur capacity of nickel(II)-zeolites were due to π-complexation.

Shiraishi et al. [1] investigated a desulfurization process of light oil, based on the formation of sulfimides by the imidation of sulfur compounds using chloramine T (sodium N-chlorotoluene -p-sulfimide) in the presence of MeOH and AcOH. On using this technique, the sulfimide of DBTs, having alkyl subsistuents, remain in the resulting light oil owing to their high hydrophobicity. These sulfimides were removed from the light oil by subsequent adsorption using aluminum oxide and silica gel due to their higher polarity as compared to the other constituents of the light oil.

In (2003) Shiraishi et al. [5] investigated the use of an imidation agent, which is insoluble in the solution in place of chloramine T. They found that by the combination of the imidation and adsorption processes, the sulfur concentration of light oil (2000 ppm) can be decreased successfully to less than 500 ppm (deep desulfurization level).

The present work focuses on investigating the feasibility of using a locally synthesized polymer–supported imidation agent (PI) for the desulfurization of two kinds of locally available light diesel oil with different sulfur contents. The activity of the synthesized PI was studied and compared with that of chloramine T.

2. *Experimental Work*

2.1 Materials:

N-tetradecane solution containing DBT (11 mmol/ℓ) corresponding to a sulfur content of 0.05 wt% was used as a model light oil. Two kinds of diesel oils were used; their properties are listed in table (1):

Table (1): Physical Properties of Diesel Fuels

Property	Al Daura diesel	Baiji diesel
Sp.gr at 15.6 (^{o}C)	0.865	0.8337
Flash point (^{o}C)	108	105
API	31.9	37.4
Sulfur content (wt%), (ppm)	(1.2354), (12354)	(0.19), (1900)

Chloramine-T was used in the desulfurization process.

2.2 Preparation of polymer supported imidation agent (PI)

The polymer supported imidation agent (PI) was synthesized according to a modified procedure based on that presented by Bogocezk and Kocioleck-Balawejdar [6] which consists of three stages as follows:

Stage I: Preparation of Polystyrene Sulfonyl chloride

In a 500-ml 3-necked flask a solution of chlorosulfonic acid ($ClSO_3H$) in dry dichloroethane (DCE) was placed and cooled to 0 ^oC in crushed ice. The mixture of polystyrene and DCE was introduced from the dropping funnel drop wise at such a rate that the temperature of the well stirred mixture does not rise when all the mixture has been added about 1 hr. The reaction mixture was stirred until the temperature of the reaction mixture reached the room temperature; the mass has swelled completely and has a light brownish color. With continuous stirring, the temperature was increased to 80 ^oC, then the mixture was allowed to stand for 24 hours with reflux condenser attached to the flask in order to complete the reaction. In order to remove the excess chlorosulfonic acid, the products were introduced into glacial acetic acid and washed with ether after filtering with suction and dried under vacuum at 50 ^oC [7].

Stage II: Preparation of Polystyrene Sulfonamide

The product of stage I (polystyrene sulfonyl chloride) was introduced into excess of aqueous ammonia solution. The mixture was stirred for 24 h at room temperature. After the product had been filtered with suction, it was thoroughly washed with water and dried under vacuum at room temperature. The polystyrene sulfonamide was obtained in the form of yellow beads [7].

Stage III: Preparation of Sodium N-chloro-polystyrene sulfonamide

The polystyrene sulfonamide that has been prepared in stage II was mixed with NaOCl aqueous solution at room temperature for 10 hr. The PI obtained (light yellow powder) was washed several times with water and dried under vacuum at room temperature. The PI was confirmed to be insoluble to most polar and non polar solvents (n-hexane, benzene, toluene, $CHCl_3$, acetonitrile, DMSO and DMF) [8].

The surface area and the bulk density of the prepared PI were measured in the Laboratory of Petroleum Research and Development Center using surface area analyzer, they were 34.02 m^2/g and 0.6994 g/cm^3 respectively.

2.3 Experimental Procedure and Analysis

(a) Desulfurization using Chloramine T

The desulfurization of n-tetradecane as a model light oil was investigated using chloramine T, according to the method applied by Shiraishi et al.[1], and as follows: n-tetradecane solution (50 ml) containing DBT (11 mmol/ℓ), corresponding to a sulfur content of 0.05 wt% was used as a model light oil. The required amount of chloramine T (0.59 g) was dissolved in 10 ml of alcohol solution and then added to n-tetradecane solution at 323 K. Small amount of AcOH (1 ml) was added to the mixture and stirred at 323 K for 24 h. Both MeOH and chloramine T are insoluble in the non-polar tetradecane. The resulting tetradecane was recovered easily using a separation funnel. A similar procedure was applied for the desulfurization of two kinds of commercial diesel oils with different sulfur contents. The MeOH solution (50 ml) containing chloramine T was then added to the light oil (50 ml) in the presence of (2ml) AcOH, and was stirred at 323 K.

(b) Desulfurization using PI

The desulfurization procedure is almost the same as that used for chloramine T. The desulfurization procedure was applied for both model light oil and commercial diesel oil and as follows: Light oil (n-tetradecane or diesel oil) 50 ml was mixed vigorously using MeOH (50 ml) with a magnetic stirrer and heated to 323 K. The PI and AcOH were then added carefully to the mixture. Following stirring for the required contacting time, the mixture was cooled to room temperature. The resulting PI was recovered by filtration. The light oil was separated from the MeOH solution and washed several times with water.

The DBT concentration in model light oil was analyzed by Gas Chromatography while the sulfur concentration of actual oil was determined by x-ray fluorescence analyzer, and IR spectra were measured using FT-IR infrared spectrophotometer on KBr disks.

The removal efficiency of sulfur compounds was calculated as the ratio of sulfur concentration that was adsorbed by the PI to the initial sulfur concentration of the commercial diesel oil that used.

$$\eta\% = \frac{C_o - C}{C_o} \times 100 \qquad\qquad \text{................................. (1)}$$

3. *Results and Discussion*

3.1 *Identification of PI (sodium N-chloro-polystyrene sulfonamide)*

The IR spectra of the synthesized stages of PI is shown in Figure (1, a,b,c). In such spectra the PI shows absorption band at (≈ 1126 cm^{-1}) and (1380 cm^{-1}) owing to S=O bonding and absorption band at (1200 cm^{-1}) owing to aliphatic hydrogen on polystyrene and absorption band at (≈ 1413 cm^{-1}) owing to S$-$OH bonding and absorption band at (≈ 1637 cm^{-1}) owing to N$-$H bonding. These results are in good agreement with the findings of Bogocgek and Kociolek-Balawejder [6].

3.2 *Desulfurization of Model Light Oil*

Figures (2) shows the results for the time course variation in the concentration of DBT in n-tetradecane (model light oil), using chloramines-T and PI in the presence of MeOH and AcOH at constant temperature of 323 K and constant initial sulfur concentration of 500 ppm. The trend of the results indicates that the sulfur content in the model light oil decreases with time and indicate that the rate of the DBT desulfurization obtained using the PI is relatively lower than that obtained using chloramine T. This is because the imidation of DBT by the PI occurs in a heterogeneous system. However, almost all the DBT in the model light oil could be removed successfully after 8 hours, thus suggesting that the PI is potential for the desulfurization of DBT.

Figure (3) shows an IR spectrum for the PI recovered following desulfurization. It shows a distinctive absorption band at (915 cm^{-1}) owing to S−N bonding, which is consistent with that for sulfimide of DBT synthesized by standard procedure.

3.3 Desulfurization of Commercial Diesel Oil

Figure (4) shows the results of the desulfurization process for Al Daura diesel on using chloramine-T and PI at constant temperature of 323 K and constant sorbent dose of 0.1 (mg/ℓ). The results indicate that the sulfur concentration decreases sharply at first but saturation is almost obtained at time greater than 12 hr.

Figure (5) shows a similar trend for Baiji diesel, but the saturation was obtained beyond 20 hr treating time for both chloramine-T and PI. The results of figures (4) and (5) indicate that neither chloramine T nor PI, at sorbent dose of 0.1 (mg/ℓ) can decrease the sulfur concentration of actual diesel oil to the deep desulfurization level.

Figures (6) and (7) show the effect of changing sorbent dose on the residual sulfur concentration in Baiji diesel and the desulfurization efficiency after 40 hours contact time using PI as sorbent.

As shown in these figures the desulfurization efficiency increases in direct relationship due to increasing sorbent dose. This is due to the increase in surface area, and hence more active sites are available for the adsorption of sulfur.

At sorbent doses beyond 0.25 mg/ℓ, the deep desulfurization level can successfully be achieved.

Figures (8) and (9) illustrate the effect of initial sulfur concentration (C_o) in commercial diesel oil on the residual sulfur content and the total removal efficiency of sulfur respectively, after 40 hours contact time and using PI as sorbent. The results indicate that the residual sulfur content increases and the removal efficiency decreases when the initial sulfur content in the commercial diesel increased for constant sorbent dose. This is probably due to the fact that for lower sorbent dose, the

total available adsorption sites are limited, but increased on increasing sorbent dose.

Although the efficiency is relatively much higher for Baiji diesel but the reduction in sulfur content for both oils is almost the same ≈1700 ppm.

3.4 Removal Efficiency Correlation

Sulfur removal efficiency is a critical parameter in the desulfurization process. The experimental results indicated clearly that the removal efficiency (η), is a function of sorbent dose and the initial sulfur concentration. An empirical expression for the removal efficiency in terms of these two parameters was proposed as follows:

$$\eta \% = a\,(Ws)^b\,(Co)^c \qquad \text{................................. (2)}$$

Based on the experimental results, STATISTICA software was applied to evaluate the empirical constants, a, b, and c, respectively. An implicit non-linear numerical method, Quasi-Newton method, was used as regression method. Initial values and step sizes were automatically allocated by the software. In this regression, second-order (partial) derivatives of the loss function were used to determine iteration steps. Convergence is achieved when the difference between consecutive iteration calculations is less than a preset criterion. The differences between experimental data and corresponding calculated results, or residual value, indicate the reliability of correlation. Small and randomly distributed residual values are desired for a valid regression. Therefore, determination coefficient, R, is used to quantify the accuracy of regression. A correlation is regarded as accurate when R is greater than 0.90. Equation (2) can be then rewritten as :

$$\eta \% = 16358.2\,\left(W_s\right)^{0.52}\,\left(C_o\right)^{-0.62} \qquad \text{-----------------------(3)}$$

The correlation coefficient, R=0.998

Figure (10) is 3-D Efficiency Profile and the relationship between Observed and Predicted Efficiency is shown in figure (11).

The effectiveness of the desulfurization process can also be represented in terms of the residual sulfur concentration. Using the same technique the residual sulfur concentration in the treated oil can be estimated from the following formula:

$$C = 0.0112 \left(C_O\right)^{1.24} \left(W_s\right)^{-0.90}, \ R=0.99974$$

4. *Conclusions*

A polymer supported imidation agent was synthesized successfully. FT-IR technique was used to identify the PI structure and it was found to be identical with the standard. A complete removal of sulfur compounds from model light oil using chloramine T and PI was achieved after 4.5 hr and 8 hr respectively. The desulfurization efficiency was found to be increasing on increasing sorbent dose and reducing initial sulfur concentration in diesel oil. Deep desulfurization level could be successfully achieved for Beji diesel oil using PI at ambient conditions and at sorbent dose beyond 0.25 (mg/ℓ). Empirical correlation for the estimation of percentage removal efficiency in terms of the major operating parameters was proposed with 95% confidence level.

Nomenclatures

Symbol	Definition	Unit
a,b,c	Empirical constants	[-]
C	Residual sulfur concentration	Ppm
C_o	Initial sulfur concentration	Ppm
R	Correlation Coefficient	[-]
W_s	Sorbent dose	mg/ℓ
η	Removal efficiency of S-compounds	[%]

Abbreviations

DBT	Dibenzothiophene
MeOH	Methanol
AcOH	Acetic acid
PI	Polymer supported imidation agent

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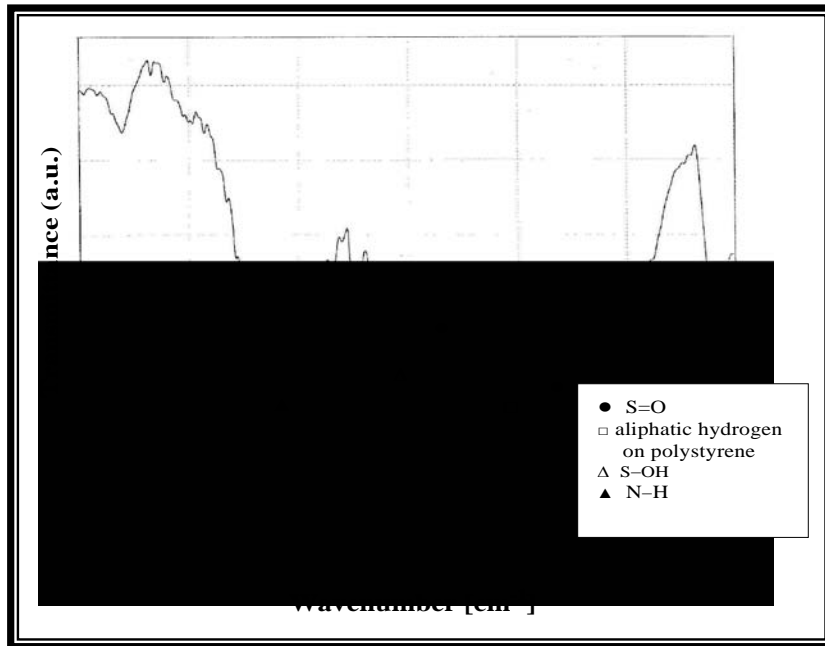
(a)   (b)

Legend:
- ● S=O
- ▢ aliphatic hydrogen on polystyrene
- △ S–OH
- ▲ N–H
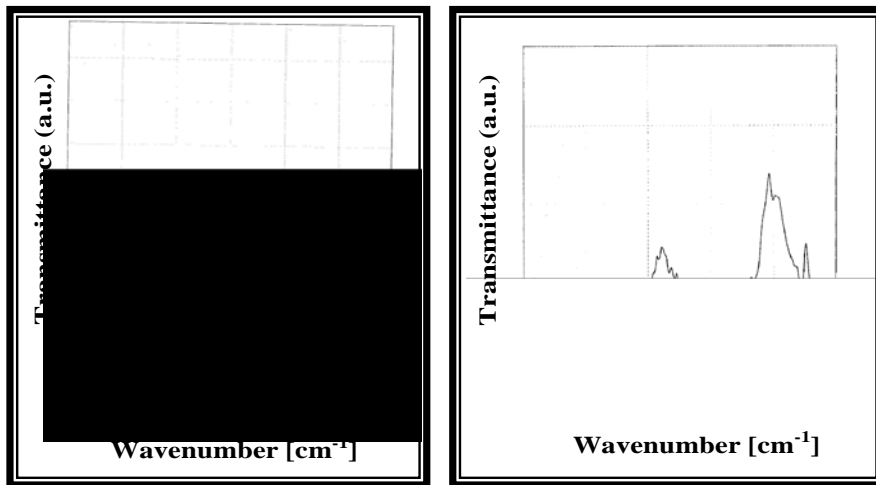
Figure.(1): IR Spectra for

(a): Poly Styrene Sulfonyl Chloride,

(b): Polystyrene Sulfonamide,

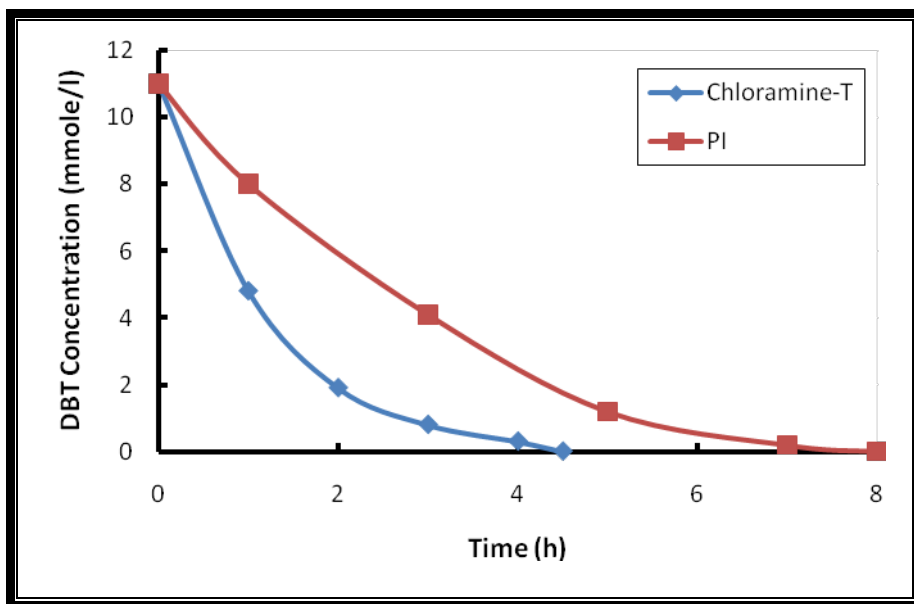*(c): Sodium N-Chloro-Polystyrene*

Sulfonamide (PI)

Figure (2): Time–course variation in the concentration of DBT in model light oil
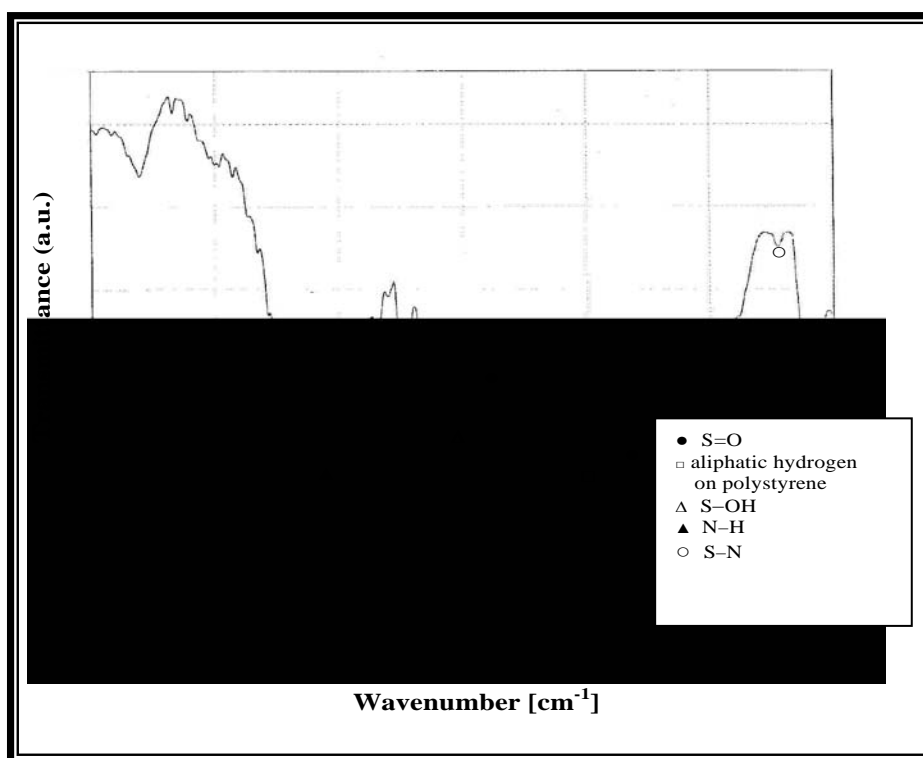

- ● S=O
- □ aliphatic hydrogen on polystyrene
- △ S–OH
- ▲ N–H
- ○ S–N

Wavenumber [cm⁻¹]

Figure (3): IR Spectra for The PI Recovered Following 8 h of Reaction in Model Light Oil / MeOH Solution in Presence Of AcOH
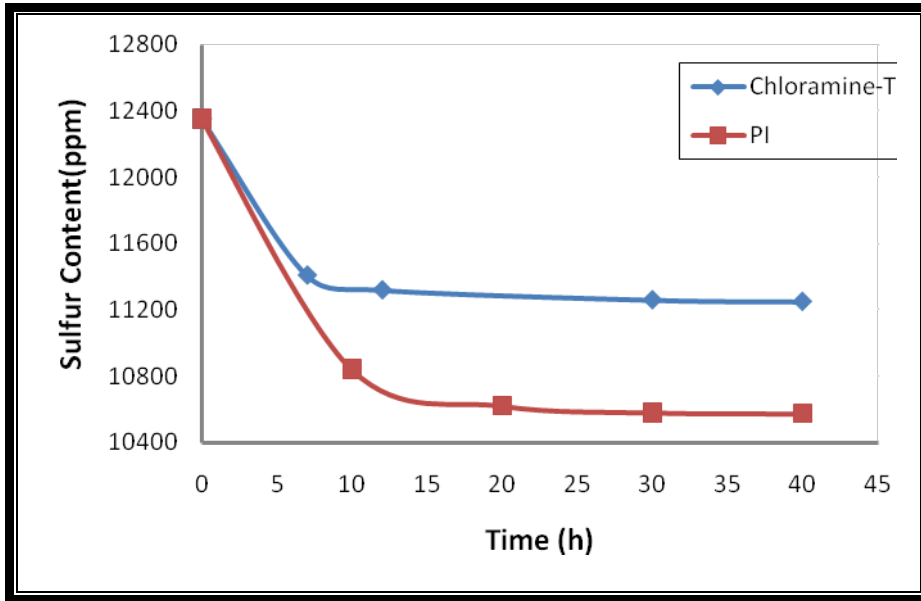
Figure (4): Time – Course Variation in The Sulfur Concentration for Al Daura Diesel
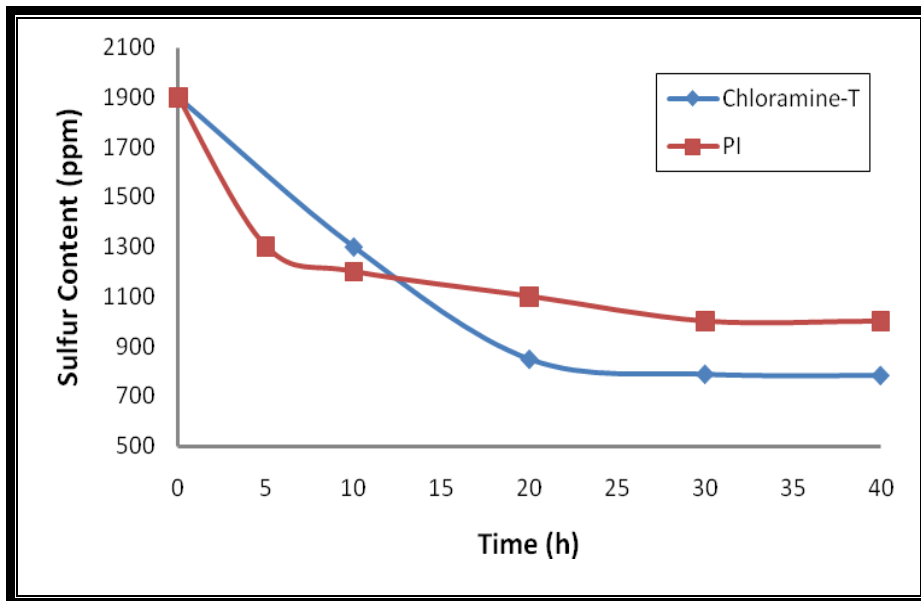
Figure (5): Time – course variation in the sulfur concentration for Baiji diesel
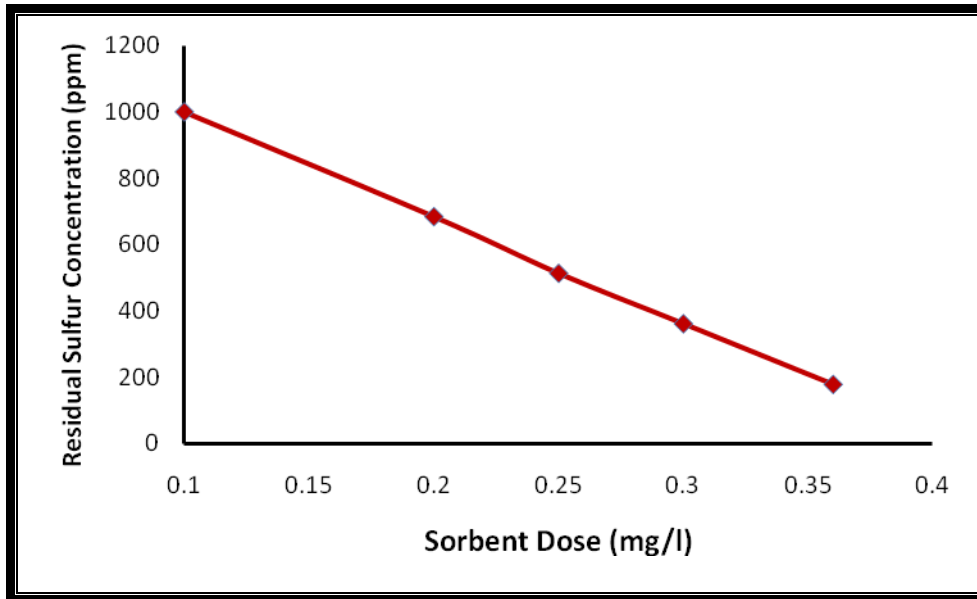
Figure (6): Residual Sulfur Content vs. Sorbent Dose
for Baiji Diesel
(PI as sorbent, t =40 h, C_o =1900 ppm)
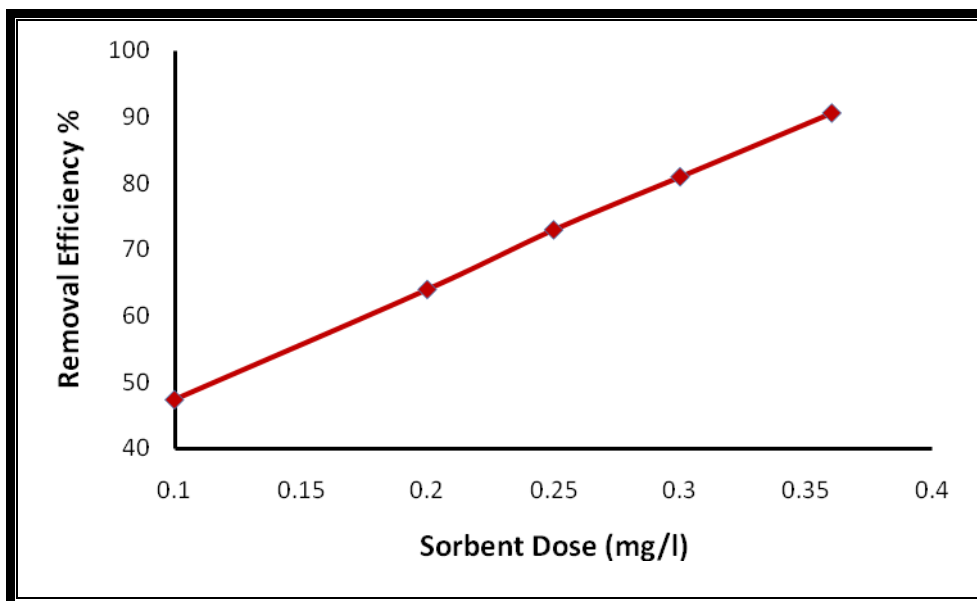
Figure (7): Desulfurization Efficiency vs. Sorbent Dose
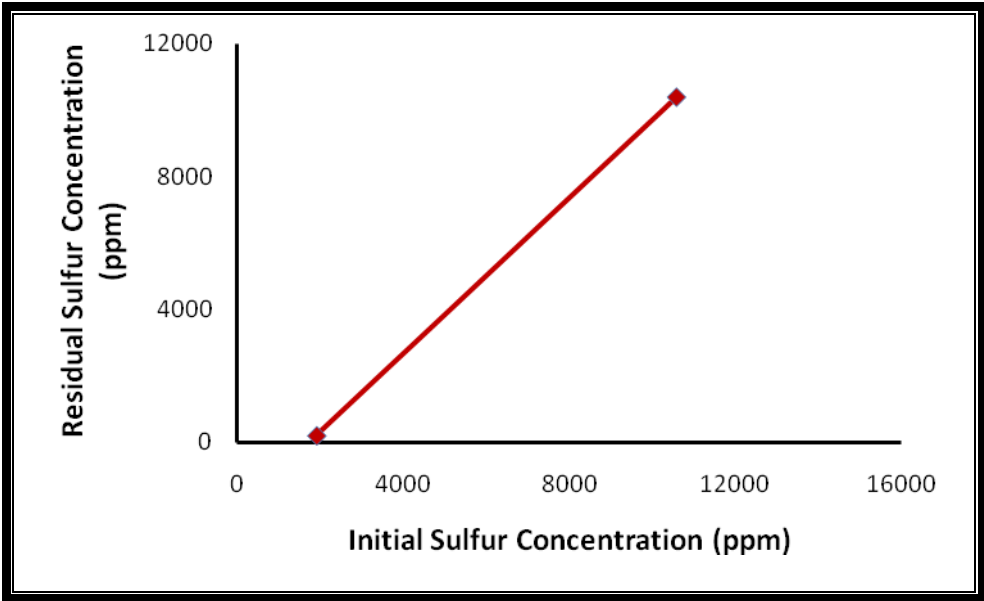*for Baiji Diesel*
(PI as sorbent, t =40h, C_o =1900 ppm)

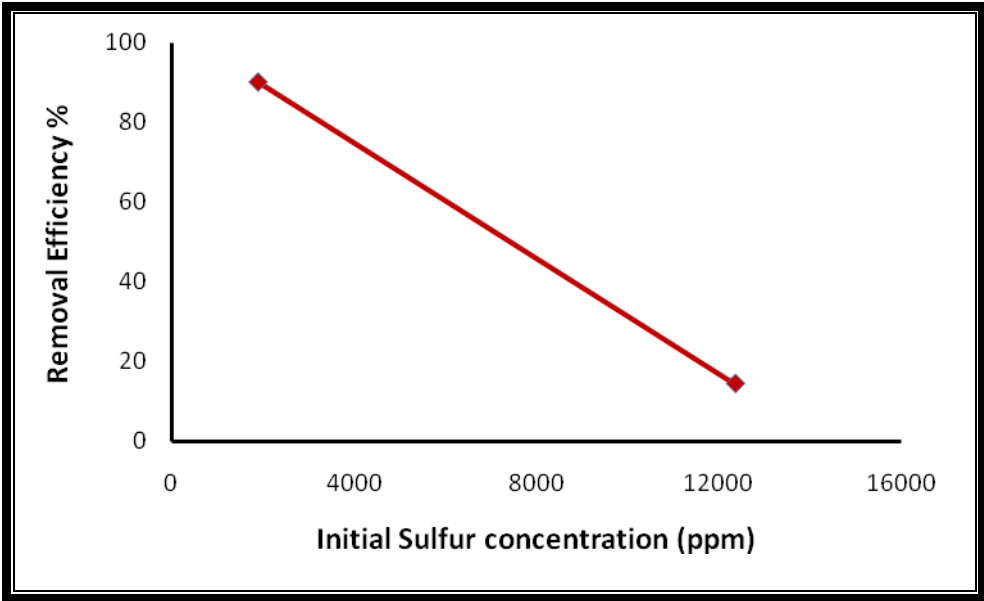*Figure (8): Residual Sulfur Content vs. Initial Sulfur Concentration*

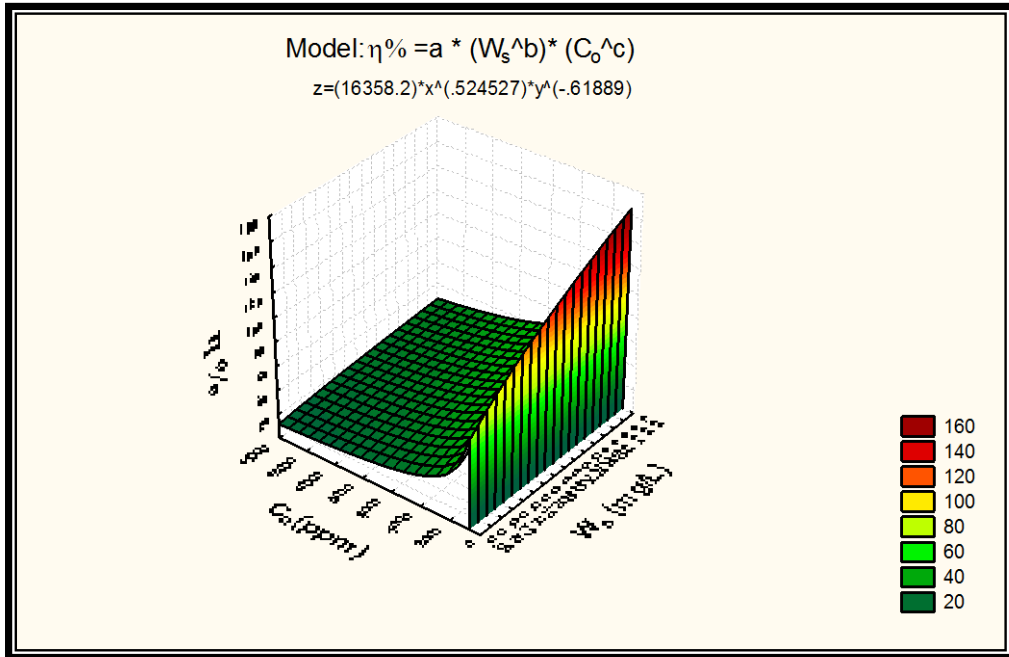*Figure (9): Sulfur Removal Efficiency vs. Initial Sulfur Concentration*

Model: $\eta\% = a * (W_s\text{^}b) * (C_o\text{^}c)$

$z = (16358.2) * x\text{^}(.524527) * y\text{^}(-.61889)$
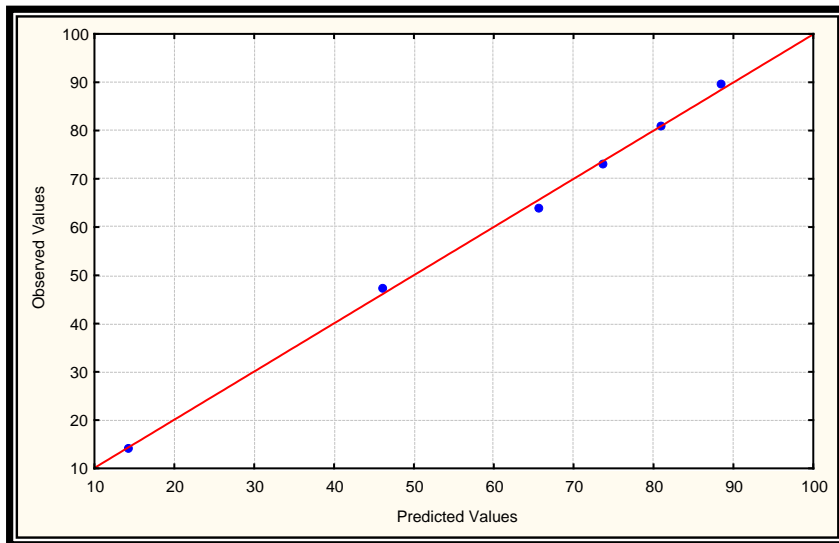
Figure (10): 3-D Efficiency Profile

**Figure (11) Relationship Between Observed
and Predicted Efficiency**