

# Scope of Adsorption in Desulphurization of Different Fuels

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**Abstract:** *Present paper reviews on sulphur removal from different fuels. Adsorption process is used to removal of sulphur from different fuels such as diesel, gasoline, kerosene crude oil and hydrocarbon fuels. Different investigators were used adsorption method for removal of sulphur by using different activating agents. Some of them were carried out batch process for sulphur removal and many of them were used continuous operation at room temperature and at atmospheric pressure. Effect of contact time, adsorbent dose, temperature, and concentration were studied by different authors. Evaluated parameters and equilibrium data were described by different isotherm model by different investigators.*

**Keywords:** Adsorption, Fuel, Desulphurization, Activated carbon

## 1. Introduction

Sulfur content of fuel has been decrease to low levels by environmental regulation in worldwide with the aim of improving air quality [A.Khodadadi]. Sulphur removal from fuels has become a very important and active subject worldwide in past decade. [Mansoor Ambia]. Environmental regulations all over the world are becoming more restrictive concerning the release of atmospheric pollutants associated with the flue gases of combustion systems. Particularly the emission of sulphur dioxide. Hence the need for producers to improve their existing technology. [Adeyi]. The high reduction in sulphur will definitely improve the emission quality and reduce the harmful effect of combustion process of diesel fuel to the environment. [Isam]. Sulphur and its organic homologues are undesirable in the liquid fuels due to the cause of environmental pollution and hindrance in variety of refining process [M.Shakirullah]. Pollutant such as exhaust gases cause damage to human health and safety of other living organisms. Diesel, a derivative of petroleum is one of the major pollutants of air, water and soil. It is rapidly increasing every year causing grave and irreversible consequences [Abel]. Production of clean hydrocarbon fuels with low sulfur and aromatic content has become one of the most important tasks of a modern petroleum refinery [Neran]. Sulphur containing compounds in heavy crude oils are undesirable in refining process as they affect the quality of the final product. Cause catalyst poisoning and deactivation in catalytic converters as well as causing corrosion problems in oil pipelines, pumps and refining equipment aside environmental pollution from their combustion and high processing cost [Abdullahi]. Thus the conditions that control the transportation of oil have become increasingly important due to the presence of sulphur so that the separation of sulphur from crude oil is one of the central requirement in most refineries and the price of oil is the identified by the amount of sulphur. [Sajma Jadoon].

## 2. Removal of sulphur from different fuels

### I. Crude oil

A. A. Adeyi et.al Kinetics Analysis and Dosage Effects of Manganese Dioxide Adsorbent on Desulphurization of Crude Oil. They were noticed that 49% reduction sulphur content of

crude oil after the process. Authors were used pseudo-second-order reaction model better described the desulphurization process. Manganese dioxide was used as an adsorbent agent in batch adsorptive desulphurization experiments. Fluorescence spectrophotometer was used to determine the remaining sulphur in each sample after adsorption [1]. Comparative Analysis of Adsorptive Desulphurization of Crude Oil by Manganese Dioxide and Zinc Oxide was studied by Adeyi and Abel. Desulphurization of crude oil was carried out by using metal oxides like activated manganese dioxide and activated zinc oxide. Authors were observed that activated manganese dioxide proved to be more efficient during the adsorption of sulphur compounds from crude oil when compared to activated zinc oxide. Investigators were used pseudo-second-order model which were fitted for the balance analysis of the adsorptive desulphurization. Finally they were proved that Langmuir model was best for activated manganese dioxide and Freundlich model was for activated zinc oxide [2]. Liu Lin et.al progress in the Technology for Desulfurization of Crude Oil he poor quality of crude oil. Authors were studied different new technologies for desulfurization of crude oil such as biodesulfurization, hydrogenation bacterial catalysis, the microwave-catalytic hydrogenation, and oxidative desulfurization in electrostatic fields, and the ultrasonic/microwave-catalytic oxidation applied in our lab, with their development trends was also described [3]. Solat et.al Methods for desulphurization of crude oil. Authors were studied and reviewed on different desulfurization methods such as oxidative desulfurization, adsorptive desulfurization, and desulfurization by photo oxidation, hydro desulfurization, desulfurization by extraction, c-alkylation, s-alkylation, microbe desulfurization, and desulfurization by ultrasound oxidation, aerobic microbe desulfurization, anaerobic microbe desulfurization and supercritical water desulfurization [4].

### II. Kerosene

Yoshie Shimizu et.al Adsorptive removal of sulphur compounds in kerosene by using rice husk activated carbon. They were used rice husk activated carbon for desulphurization of kerosene upto 77 % The capacities of rice husk activated carbons to adsorb refractory sulfur compounds of dibenzothiophenes were evaluated by

investigators for correlating with their textural and chemical characteristics[5]. Ultrasound-Assisted Desulfurization of Commercial Kerosene by adsorption was studied by Mahesh patil. Author was investigated Sorption of hexyl mercaptan sulfur onto carbon-based adsorbents by ultrasonic irradiation. Investigator was observed that Carbon nanotubes showed higher adsorptive capacity [6].

### III. Gasoline

Jingwei Rui et.al “Adsorptive Desulfurization of Model Gasoline by Using Different Zn Sources Exchanged NaY Zeolites” Authors were prepared NaY zeolites by the liquid-phase ion-exchange method with different Zn sources, including  $Zn(NO_3)_2$ ,  $Zn(Ac)_2$  and  $ZnSO_4$ . Investigators were investigated that the regenerated  $Zn(Ac)_2$ -Y adsorbent afforded 84.42% and 66.10% of the initial adsorption capacity after the first two regeneration cycles and they were observed that a sample of  $Zn(Ac)_2$ -Y, prepared by an ion-exchange method with  $Zn(Ac)_2 \cdot 2H_2O$  as a precursor, exhibited the highest capacity for sulfur removal. Finally authors were concluded that the sulfur adsorption capacity decreases with the increase of the adsorption-regeneration cycle due to the low zeolite framework stability of the Zn cations [7].

Desulfurization of heavy oil was studied by Rashad Javadli and Arno de Klerk. Authors were studied different desulfurization techniques for heavy oil. They were observed that the fouling nature, high viscosity, and bulkiness of the molecules in heavy oil undermine the efficiency of processes that require a solid material, as catalyst or adsorbent. Authors were concluded that autoxidation was a viable desulfurization strategy for heavy oil [8].

The reactive adsorption desulfurization of model gasoline was carried out on Ni/ZnO-HY adsorbent by Huang Huan and Salissou M. Nour using Ni/ ZnO-HY adsorbent. Authors were investigated that Ni/ZnO-HY adsorbent showed the best desulfurization performance. They were proved that 92.19% of sulfur was recovered using Ni/ZnO-HY adsorbent and would be maintained at 82.17% of the fresh one after 5 regeneration cycles [9].

Mansoor and Sajedeh was studied desulfurization of gasoline using novel mesoporous carbon adsorbents. They were prepared mesoporous carbon adsorbents from spherical SBA-16 mesoporous silica, as a template. Investigators were found that the amount of DBT adsorption on OMC is higher than SBA16. The synthesized materials were studied by X-ray diffraction, scanning electron microscopy and nitrogen adsorption-desorption isotherms [10].

Xiao Chen et.al. Mossbauer spectroscopic characterization of ferrites as adsorbents for reactive adsorption desulfurization. Authors were synthesized nanocrystalline ferrite adsorbents from metal nitrates and urea using a microwave assisted combustion method. They were carried out adsorption experiments using a fixed bed reactor to evaluate the ADS reactivity and concluded that prepared  $AFe_2O_4$  were effective adsorbents for the reactive ADS of model gasoline [11].

### IV. Hydrocarbons

M.S.Patil et.al Sorption of sulfur onto activated carbons by batch reactor. They were used black liquor for preparation of activated carbon. They were carried out batch operation Adsorptive desulfurization of the model fuel Authors were observed that activated carbon was found to have highest adsorption capacity and experimental data obtained was obeyed Langmuir adsorption isotherm model [12]. Selective sulphur removal from liquid hydrocarbons over regenerable  $CeO_2$ - $TiO_2$  adsorbents for fuel cell applications was studied by Shingo Watanabe, Xiaoliang Ma and Chunshan Song. Authors were studied the effect of Ti-Ce atomic ratio on the adsorptive performance of the Ti-Ce bimetal oxide adsorbents ( $TiO_2$ - $CeO_2$ ) and the regenerability of the TiCe bimetal oxide adsorbents. Investigators were concluded that the bi-metal oxides showed better adsorptive performance than the monometal oxides,  $CeO_2$  and  $TiO_2$ [13].

### V. Model oil

Muhammad Ishaq et.al. Adsorptive desulfurization of model oil using untreated, acid activated and magnetite nanoparticle loaded bentonite as adsorbent. Investigators were used novel ultraclean adsorption desulfurization process for model oil using untreated, acid activated and magnetite nanoparticle loaded bentonite as adsorbent. They were conducted batch experiments for study the effect of contact time, adsorbent dose, initial dibenzothiophene, concentration and temperature. Investigators were investigated that the bentonite impregnated with magnetite exhibits better performance in the desulfurization of fuel as compared to bentonite in untreated form as well as activated with  $HNO_3$ [14]. Desulfurization of Model Oil via Adsorption by Copper (II) Modified Bentonite was studied by Dezhi Yi, Huan Huang, and Li Shi. Authors were carried out desulfurization process by adsorption for removing dimethyl sulfide and propylmercaptan using bentonite adsorbents modified by  $CuCl_2$ . Investigators were observed that the maximum sulfur adsorption capacity obtained at a Cu(II) loading of 15 wt %, and the optimum calcination temperature was 150 °C[15]. M. Shalirullah et.al Desulphurization of liquid fuels by selective adsorption through mineral clays as adsorbent. Authors were carried out batch experiments for desulphurization. they were used clays collected from local sources, including Kaolinite, Montmorillinte, Palygorskite and Vermiculite as an adsorbent. Investigators were observed that Kaolinite exhibited the maximum desulphurization yield of 60 %, 76 % and 64 % at 6 hrs adsorption incase of crude oil, kerosene and diesel oil respectively[16].

### VI. Diesel

Marko Muzic et.al Kinetic, equilibrium and statistical analysis of diesel fuel adsorptive desulphurization” Authors were carried out adsorption experiment for determination of parameter like influence of time, initial sulfur concentration, activated carbon mass and their interactional effects on sulfur content and adsorption capacity by using activated carbon and activated aluminium oxide. They were observed that activated carbon was efficient during the adsorption of sulfur compounds from diesel fuel when compared to aluminium oxide[17]. Deep Desulfurization of Diesel Fuel by Guard Bed

Adsorption of Activated Carbon and Locally Prepared Cu-Y Zeolite was studied by Nada Mustafa Hadi. Investigators were carried desulfurization of diesel by different adsorbents in a fixed bed adsorption process operated at ambient temperature and pressure. Authors were proved that when Cu Y-zeolite adsorbent used with activated carbon as a guard bed, Cu-Y zeolite provides by for the best adsorption capacities both at breakthrough point and at saturation [18]. A Review on Bio- and Adsorptive Desulfurization of Diesel Fuel was studied by Mojirade, Aribike and Nwachukw. Authors were studied the potentiality of ADS of real and model diesel using different adsorbents types like nano particles and different types of clays impregnated with different chemical precursors and sewage sludge[19].S. Zheng et.al. Mesoporous and Macroporous Alumina-Supported Nickel Adsorbents for Adsorptive Desulphurization of Commercial Diesel. Authors were prepared High-performance adsorbents using mesoporous and macroporous alumina for adsorptive desulphurization of commercial diesel at atmospheric pressure. Investigators were used nitrogen adsorption isotherms (BET), X-ray diffraction, scanning electron microscopy, high-resolution transmission electron microscopy, temperature-programmed reduction of hydrogen, temperature-programmed desorption of ammonia and Fourier transform infrared techniques for characterization of adsorbents[20]. New methods of removing sulfur from commercial diesel using surfactants and micro emulsion systems was developed by Castro Dantas and Dantas Netontas Investigators were carried out Batch adsorption tests to assess the ability of vermiculite to adsorb sulfur from diesel. Authors were investigated that the vermiculite adsorbed 4.24 mg of sulfur/g of adsorbent, corresponding to 68.7% sulfur removal. And the process yielded 46.8% sulfur removal in the two-stage experiment and 73.15% in the six-stage experiment [21]. Khodadadi et.al Adsorptive desulfurization of diesel fuel with nano copper oxide (CuO).They were carried out adsorption experiments for desulphurization. Authors were used CuO nano particle as adsorbent for the desulfurization of liquid fuels and investigate its characterization[22].Desulfurization of Diesel Fuels by Adsorption via  $\pi$ -Complexation with Vapor-Phase Exchanged Cu(I)-Y Zeolites was studied by Arturo J, Hernandez-Maldonado and Ralph T. Yang.Authors were investigated that the sulfur adsorption capacity was increased by 14% after a thin layer of activated alumina was placed on top of a fresh zeolite bed And they were showed that activated aluminas are capable of adsorbing large thiophenic molecules, but not too deep desulfurization levels[23].Nguyen Thanh et.al desulfurization of raw diesel fuel by metal-modified mesoporous silica. Authors were prepared Metal-modified mesoporous silica adsorbents to selectively remove sulfur compounds from diesel fuel having conc. 470 ppmw. Investigators were investigated that the maximum removal percent for sulfur compounds were 57.5% with MCF-Ti-20 adsorbent. And the initial adsorption rate of sulfur compounds on metal modified MCF was faster than MCF adsorbent and the adsorption rates in all of the adsorbents equal zero after 400min[24].Adsorptive desulfurization of diesel fuel was investigated applying two Design of Experiments methods was investigated by M. Music, Sertia-Bionda, and. Gomzi. The experiments were carried out in a batch adsorption system using Chemviron Carbon SOLCARBTM C3 activated carbon as adsorbent

Adsorptive desulfurization of diesel fuel was investigated by applying two DOE methods, three factor two-level factorial design. Investigators were investigated that the lowest achieved output sulfur concentration was 7.6 mg kg<sup>-1</sup> with relatively low sorption capacity of 0.0861 mg g<sup>-1</sup>[25].The microwave-assisted adsorptive desulfurization of model fuel was investigated using a synthesized rare earth metal-doped zeolite by N. Salahudeena and A.S. Ahmeda. They were investigated that the synthesized zeolite was effective for adsorptive desulfurization of a model fuel, having the best efficiency of 75% in a microwave-assisted desulfurization carried out at 100 °C for 15 minutes [26]. Neran and Samar were studied a batch adsorption desulfurization process for diesel fuel containing 580 ppm sulfur, based on physical adsorption of refractory sulfur compounds on activated carbon. They were studied effects of time, temperature, diesel to AC ratio, AC particle size, mixing velocity, and initial sulfur concentration in commercial diesel fuel on the desulfurization efficiency. Authors were investigated that the residual sulfur concentration in diesel fuel was decreased from 580 to 247 ppm, corresponding to a desulfurization efficiency of 57% [27]. A. R. Lope's et.al Palladium Loaded on Activated Carbon for Sulphur Compounds Adsorption in Commercial diesel. Authors were conducted adsorption process and batch tests were performed to compare the adsorption capacity for palladium supported carbon and unmodified activated carbon. The study was conducted to determine the parameters of adsorption seeking approximate actual conditions existing in the production of diesel. They were investigated that the adsorption capacity of palladium supported carbon was 120% superior for sulfur compounds [28].Olatunji et.al Total Sulfur Levels in Refined Petroleum Products of Southwestern Nigeria Using UV/VIS Spectrophotometer. They were investigated that the sulfur concentrations in the analyzed fuel samples were 0.0019–0.0178wt% for gasoline and 0.027–0.169 wt% for diesel. Authors were observed that the sulfur levels in the selected samples were below the Nigerian standard for gasoline and diesel while 89.9% of the samples exceeded the U.S. Environmental Protection Agency standard [29]. Hamda et.al selective adsorptive desulfurizations of diesel fuel on carbon nanospheres. Authors were studied sulfur removal to acceptable levels by using a selective adsorptive desulfurization process at room temperature and atmospheric pressure. They were used carbon nanospheres as good adsorbent for the desulfurization of liquid fuels. Authors were investigated that the efficiency of removing sulfur from diesel fuel by the adsorption process with CNSs adsorbents was found to be 87% [30].Adsorptive Desulfurization of Commercial Diesel oil Using Granular Activated Charcoal was studied by Isam and Noora. They were investigated adsorption of sulfur compounds form commercial diesel oil on a granular activated charcoal. Investigators were investigated that the adsorption desulfurization of diesel oil using GAC showed good efficiency for sulfur removal of 20.94% at room temperature [31].Desulfurization of Gasoline and Diesel by Adsorption with Cu(I)-Y Zeolite by studied by Kuen Song. Authors were fabricated Cu(I)-Y zeolite nanoparticles for the desulfurization of commercial gasoline and diesel using fixed-bed adsorption processes at room temperature. Investigators were demonstrated that organic sulfur compounds in gasoline and diesel fuel can be removed by selective adsorption using a transition metal



compound loaded on a porous support [32]. Gaurav Daware et.al Desulphurization of diesel by using low cost adsorbent. Investigators were used neem leaves powder as an adsorbent for the adsorption desulphurization process of diesel fuel. Authors were carried out batch experiments for effect of contact time, adsorbent dose, temperature, and sulphur concentration. They were investigated that maximum removal of sulphur was 65% at 20°C [33]. Isam A. H. et.al. Adsorption Process of Sulfur Removal from Diesel Oil Using Sorbent Materials. They were used commercial activated carbon and carbonized date palm kernel powder as a adsorbent for adsorption-desulfurization process of diesel fuel. They were carried batch experiments for desulphurization. Authors were investigated that the sulfur content was reduced from 410 ppm to 251 ppm using 5% adsorbent material and further reduction and up to 184.6 ppm using 10% sorbent material [34]. Desulphurization of Tawke Diesel Fuel by Adsorption on Na-Y Type Zeolite, Local Clay and Active Carbon. The removal of sulfur compounds from Tawke diesel fuel was studied by Mohammed K. Younis and Sherwan Mohammed Simo. They were used adsorbents like granular Na-Y type zeolite, MOR type zeolite, molecular sieve 3A type, local clay and activated charcoal for desulfurization process. They were investigated that the desulfurization by activated charcoal is more efficient than by the clay, zeolite type and almost reach more than 20% [35]. A Seyed et.al Review on Diesel Fuel Desulfurization by Adsorption Process. Authors were reviews on desulphurization processes by adsorption. They were observed that new synthetic sorbents and catalysts and modified clays were under research to find efficient one in each process [36]. Marko Muzica et.al Optimization of diesel fuel desulfurization by adsorption on activated carbon. Authors were used batch adsorber. For desulphurization of diesel by adsorption and they were used response surface methodology was applied for optimizing the adsorption process of organic sulfur compounds. Investigators were investigated that the overall process optimum in was reached at 50 °C and 100 minutes with input sulfur concentration of 16,0 mg kg<sup>-1</sup> and adsorbent mass of 4,00 g when sulfur concentrations of around 6,6 mg kg<sup>-1</sup> were attained [37]. Adsorptive Desulfurization of Diesel for Fuel Cell Applications was studied by Hoang Phuoc. The performances of several kinds of commercial adsorbents based on activated carbons, zeolites, and metal oxides for desulfurization of ULSD were screened by authors. They were investigated that it was possible to reduce sulfur content in commercial ULSD in Korea containing approximate 5 ppmw S to 0.1 ppmw which was the tolerance level for MCFC application the limit level 0.1 ppmw [38]. Adsorptive desulfurization and denitrogenation were studied by Jae Hyung Kim using a model diesel fuel, which contains sulfur, nitrogen and aromatic compounds, over three typical adsorbents such as activated carbon, activated alumina and nickel-based adsorbent in a fixed-bed adsorption system. Authors were examined the adsorptive capacity and selectivity for the various compounds were examined and compared on the basis of the breakthrough curves [39]. G. Karagiannakis et.al Liquid phase adsorptive desulphurization of diesel fuel. Investigators were investigated that the lab-scale liquid desulfurization of commercial diesel fuel via adsorption, under ambient conditions, employing a high-surface area activated carbon

sorbent. They were also investigated several strategies for the regeneration of the partially saturated sorbent and observed that the selected sorbent was able to desulfurize a commercial diesel fuel containing total sulfur content 7.1 ppmw up to sub-ppm values [40]. Abel et.al Kinetics Analysis of Manganese Dioxide Adsorbent on Desulphurization of Diesel Oil. They were investigated Adsorptive desulphurization of diesel oil in a batch reactor using activated manganese dioxide as the adsorbent. Authors were investigated that desulphurization efficiency was found to increase with increase in contact time and there was reduction in the sulphur content of the examined diesel oil by 53% after desulphurization [41]. Adsorptive desulfurization of feed diesel using chemically impregnated coconut coir waste was investigated by J. K. Ahmed and M. Ahmaruzzaman. They were used chemically impregnated coconut coir waste for the desulfurization of feed diesel. Authors were carried out Batch experiments with feed diesel having a total sulfur concentration of 2,050 mg L<sup>-1</sup> were conducted to optimize the adsorption parameters such as adsorbent dose, temperature, and contact time [42]. Andre et.al. Pd-Impregnated activated carbon and treatment acid to remove sulfur and nitrogen from diesel. Authors were used adsorption process for removal of sulfur and nitrogen compounds from national commercial diesel through Brazilian commercial activated carbon samples which was modified by acid oxidation and, alternatively, were impregnated with palladium chloride. Investigators were concluded after adsorption that adsorption efficiency of the activated carbon impregnated with palladium chloride was over 85% for nitrogen compounds and over 60% for sulfur compounds [43].

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