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Removal of sulphur from liquid fuels using low cost Activated carbon -A review

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Abstract
This paper review on the use of activated carbon as a adsorbent which have a greater capacity to adsorb the sulfur compounds present in liquid fuel. Desulphurization by activated carbon is more efficient and low cost and excellent for adsorbent in adsorption process. Sulphur is present as an impurity in liquid fuel such as petrol, diesel, kerosene, crude oil and it should be removed from environment using different desulphurization methods. Adsorption desulfurization process is one of the easy method by using low cost and commercial activated carbon, which is very helpful in reduction of sulphur compounds from environment and its impact on surrounding.

Keywords: *Sulphur, Activated carbon, Adsorption, Adsorptive desulphurization, Liquid fuel.*

1. Introduction

Desulphurization prior to combustion has been viewed in recent years with the objective of ensuring clean fuel combustion and hence to avoid environmental degradation. Diesel is the larger and widely used source of energy in the world. However, diesel fuel contains sulphur, typically in the form of organic sulphur compounds. Sulphur is the third most abundant element after carbon and hydrogen in diesel fuel[1].Desulfurization of hydrocarbon fuels has lately become one of the most important processes in petroleum refining. Adsorption is a process that can be applied for diesel fuel desulfurization. Sulfur, as well as sulfur compounds, from crude oil and oil fractions represent a problem within the petroleum refining and related industries ever since the very beginning of crude oil refining, and with sulfur being removed the quality of a product is improved which notably attributes to the economy of oil refining[2]. Adsorptive desulfurization of diesel fuel is very essential process by using activated carbon, which has been proven as an excellent adsorbent for such a task[3].On a global scale the reduction of atmospheric emissions has encouraged environmental institutions to establish ever stricter legislation, principally in relation to the sulfur content of automotive fuels Thus, new alternatives to remove sulfur compounds have been studied in order to achieve the low levels stipulated in the new specifications without altering the quality of the product[4]. Adsorbents other than carbon in removal of sulfur from petroleum, activated carbon in some form or other is incorporated along with other adsorbents, or alternatively activated carbon is used as an adsorbent for removal of products of oxidation of sulfur compounds, as activated carbon shows higher parameter values [5].The specific activated carbon is required to have a composite micro-meso porous structure with a large pore volume. A mesoporous activated carbon, that has a micropore volume similar to the ACF but contains a considerable mesopore volume.[6,7].Adsorptive desulfurization processes are considered among the most economically attractive techniques due to their simple operating conditions and the availability of inexpensive and re-generable adsorbents such as reduced metals, metal oxides, alumina, metal sulfides, zeolites, silica, and activated carbon.[8]. Adsorptive desulfurization processes are considered among the most economically attractive techniques due to their simple operating conditions and the availability of inexpensive and re-generable adsorbents such as reduced metals, metal oxides, alumina, metal sulfides, zeolites, silica, and activated carbon[9].The zeolite-based adsorbents have been used as promising materials for selectively removing the sulfur derivatives from diesel. Metal ion exchanged Y zeolites showed high selectivity and capacity for sulfur compounds using complexation between metal ion and sulfur compounds [10]. The selectivity of the zeolite-based adsorbents varies according to fuel composition such as aromatic and moisture concentrations Activated charcoal, Clay minerals also were used to remove nitrogen and

sulfur compounds, besides their using in petroleum refinery as catalyst for cracking reactions Separation processes that are being applied for desulfurization of different petroleum fractions include adsorption, extraction and combined process of oxidation and extraction.[11].Activated carbons and zeolites have been widely used as adsorbents in the separation and purification processes for gaseous or aqueous solution systems. Activated carbons have high adsorption capacity towards some organic and inorganic compounds due to large specific surface area, high adsorbate-adsorbent physical and chemical attraction and balanced macro-meso-and micro-porosity [12]. Adsorbents can be reused by the proper regeneration process. Recently, there was a lot of interest in developing sorbents for selective adsorption of organosulfur compounds from liquid fuel. Various studies on the ADS process using different adsorbents such as activated alumina, zeolites, activated carbons, and mesoporous materials[13].

2. **Review on different types of activated carbon for sulphur removal from liquid fuels**

Gaurav et.al.used activated carbon from neem leaves for desulphurization of diesel. They were carried out batch experiment for sulphur removal from diesel at temperature283, 288 and 293K with different initial concentrations. They were used spectrophotometer for analysis of sulphur. They were studied parameter like Effect of adsorbent dose, Effect of initial concentration and time. They were showed that the sulphur adsorption capacity of the neem increases significantly with an increase in Co, but only weakly with an increase in the temperature of the solution. They were studied sorption kinetics by using the pseudo-first-order and pseudo-second-order kinetic model to fit the experimental kinetic data. They concluded that desulphurization of diesel oil by adsorption process using neem leaves powder shows a reduction in the amount of sulphur by more than half of the original amount of sulphur. The optimal conditions were recognized as contact time of 3.5hrs and dose of neem leaves powder of 2gm in 10ml of diesel at temperature of 20OC was obtained [1] .

Marco Muzic et.al. Kinetic equilibrium and statistical analysis of diesel fuel by adsorptive desulphurization. The total sulfur content in the samples of diesel fuel was determined by wave dispersive x-ray fluorescence spectrometer. Authors compared experimentally gained results to the data gained from the regression analysis via empirical kinetic models. They also compare the efficiency of removing sulfur from diesel fuel in the adsorption process with adsorbents activated carbon and activated aluminum oxide. The efficiency of removing sulfur from diesel fuel was tested using the process of adsorption. And the adsorption was conducted on activated carbon and activated aluminium oxide. Activated carbon proved to be more efficient during the adsorption of sulfur compounds from diesel fuel when compared to aluminum oxide. The balance characterization for both used adsorbents showed that the process of adsorption desulfurization was described by Freundlich model [2].

Muzic et.al was studied design experiments investigation of adsorptive desulphurization of diesel fuel.The adsorbent used was Chemviron Carbon SOLCARBTM C3 activated carbon whose initial characteristics were: particle diameter, dp, 1. Total sulfur concentration was measured using wave dispersive. Time, initial sulfur concentration and adsorbent mass were chosen as independent variables, so-called factors, and the output sulfur concentration and sorption capacity were dependent response variables. They were conducted experiments efficiently by a proper choice of design, in order to determine operating conditions according to the optimal response based on a set of controllable variables. Authors concluded that, with the increase in time and adsorbent mass, the concentration decreases while it was proportional with regard to C0 when the increase of initial sulfur concentration was causing the increase in output concentration. At the same time, sorption capacity's dependence on t and C0 was proportional, i.e. increase in t and C0 causes an increase in capacity, while it is adversely proportional with regard to mC3 when the increase of adsorbent mass is causing the decrease in sorption capacity. Adsorptive desulfurization of diesel fuel was investigated by applying two DOE methods, three factor two-level factorial design and k 3 Box-Behneken design. They were conducted experiments according to BBD and subsequent multiple regression analysis, resulted with the development of second-order model equations for predicting output sulfur concentration and sorption capacity [3].

Andre et.al. Used Pd Impregnated activated carbon for removal of sulfur and nitrogen from diesel .Brazilian commercial and modified activated carbon samples can be used for the removal of sulfur and nitrogen Brazilian commercial activated carbon samples (AC) were modified by acid oxidation and, alternatively, were impregnated with palladium chloride. They carried out experiment for the desulphurization and nitrogen removal from diesel by using activated carbon .They were used BET method for determination of surface area, pore volume and pore size. The quantification of sulfur and nitrogen compounds in the diesel was carried out using an Elementary sulfur analyzer (model Trace SN cube). Authors were concluded that Percentage nitrogen removed from the commercial diesel was above 85%. And above 60% for the removal of sulfur compounds from commercial diesel [4].

Desulphurization of hydrocarbon liquid fuels by adsorption was studied by Patil and Bhattacharyulu. They studied removal of mercaptan sulfur compound from hydrocarbon streams and hence to prepare an activated carbon of reasonable uptake capacity, for sulfur removal to be used commercially They were performed batch experiments for Sorption of sulfur onto activated carbons.Activated carbon was prepared from black liquor. Phosphoric acid and nitrogen were used as intercalating agents. Langmuir adsorption isotherm model was used for experimental data.The surface morphology of the two activated carbons before and after sulfur sorption was verified using scanning electron microscope (SEM) and X-ray diffraction studies (XRD). They were found that activated carbon have highest adsorption capacity [5].

Yoshie Shimizu et.al. Adsorptive removal of sulphur compounds in kerosene by using rice husk activated carbon.Investigators were used rice husk for activated carbon preparation.Investigators used rice husk for activated carbon preparation. The capacities of rice husk activated carbons (RHACs) to adsorb refractory sulfur compounds of dibenzothiophenes (DBTs) were evaluated correlating with their textural and chemical characteristics. Authors were concluded that the largest DBTs adsorption capacity (0.069 mg-S/g-Ads and 77 % performance to the ACF) was observed, despite much smaller specific surface area (473 m2/g) and total pore volume (0.267 cm3/g) compared to those of the ACF [6].

Adsorption Process of Sulfur Removal from Diesel Oil using Sorbent Materials has been studied by Isam A. and Al Zubaidy [1] They used Date palm kernel powder for desulphurization process for diesel fuel. They showed that Carbonized material from date palm kernel was also used but without activation for desulfurization process of diesel fuel and able to reduce sulfur content by 34.15% with the addition of 6% by mass sorbent material. 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 [7].

Adsorption of Thiophenic Compounds from Model Diesel Fuel Using Copper and Nickel Impregnated Activated Carbons was studied by Elham and Moosavi. This paper investigated the impact of selective loading of different copper and nickel species on activated carbons for adsorption of benzothiophene (BT), dibenzothiophene (DBT), and 4,6-dimethyl-dibenzothiophene (4,6-DMDBT) from single-solute model fuel solutions In this study, adsorption of refractory thiophenic sulfur compounds i.e., benzothiophene (BT), (DBT), and 4,6-dimethyldibenzothiophene (4,6-DMDBT) in single-solute systems from n-hexane solutions onto metal-impregnated activated carbons was investigated. A polyacrylonitryl-based commercial activated carbon fiber (ACF) and a mesoporous activated carbon (AC) were used in this study. Investigators were used Boehm titration method to quantify the concentration of different acidic oxygen groups of the ACFH sample. They were used isotherm for each adsorbent which represents both physio and chemisorptions uptakes The main aim of this work was to remove acidic oxygen functionalities by metal impregnation adsorbents high temperature hydrogen reduction.Authors were suggested to increase CFH isotherms shows that metal impregnation could not increase the TC uptake more than ~40%–53% (i.e., about 70% of the TC uptake by metal loaded carbons was due to the TC adsorption on the carbon surface and the remaining 30% is due to the adsorption of TC on metal sites interactions with TC[8].

Isam et.al.investigated Adsorptive Desulfurization of Commercial Diesel oil Using Granular Activated Charcoal. They examined equilibrium of sulfur adsorption on granular activated charcoal. The adsorption isotherm study was conducted and the experimental isotherm was fitted to Langmuir and

Freundlich equations. The adsorption desulfurization of diesel oil using GAC showed good efficiency for sulfur removal of 20.94% at room temperature. The kinetic study showed that the adsorption desulfurization process of diesel oil is more concise with Langmuir isotherm. Investigators were concluded that there is improvement in ignition quality, cetane number and diesel index after desulfurization of diesel [9].

Desulphurization of Tawke Diesel Fuel by Adsorption on Na-Y Type Zeolite, Local Clay and Active Carbon was studied by Mohammed K .and Mohammed Simo.They carried out experiments for the removal of sulfur compounds from Tawke diesel fuel.and used adsorbents like granular Na-Y type zeolite, MOR type zeolite, molecular sieve 3A type, local clay and activated charcoal. Authors were used EDXRF Sulfur Meter RX-360SH for sulphur content measurement. Mineralogical nature and chemical composition of clay was found by X-ray analysis. Investigators showed that the percentage of Al2O3 and SiO2 in the sample was 7.29% and 41.5%, respectively. Whereas the percentages of other metals like Fe2O3, CaO, K2O, MgO and Na2O are 9.20%, 10.38%, 0.65%, 9.82% and 0.47%, respectively. Authors were concluded that the desulfurization were increased by activated carbon more than by clay and zeolite e temperature increased, while clay and zeolite respond very little, this were probably due to the decrease of diesel viscosity for higher temperatures that favours the access to adsorption sites inside the pores.[10].

Marko Muzic et.al.analysis of Continuous Fixed Bed Adsorptive Desulfurization of Diesel Fuel .They carried out adsorptive desulfurization experiments in a fixed bed adsorption column to investigate the influence of feed flow, working temperature and bed depth on output sulfur concentration and breakthrough time, as well as for checking the fixed bed adsorption model's adequacy for predicting breakthrough curves. They were showed that by decreasing the feed flow and increasing the bed depth, the output sulfur concentration was decreased and the breakthrough time was extended. They performed kinetic analysis of the fixed bed adsorption model, resulting in predicted breakthrough curves and pertaining constants, showed that the best fit was achieved for the experimental data collected for the lowest feed flow of 1.0 cm3 min-1 when the model took in to account the mass transfer rate as the slowest process [11].

Deep Desulfurization of Diesel Fuel by Guard Bed Adsorption of Activated Carbon and Locally Prepared Cu-Y Zeolite was studied by Nada Mustafa Hadi and Sarmad Abdul Razzaq Rashid and Suheila abdalreda . They were used fixed bed adsorption process operated at ambient temperature and pressure with three different adsorption beds such as commercial activated carbon, Cu-Y zeolite, and layered bed of 15wt% activated carbon followed by Cu-Y zeolite.Initially Y-zeolite was prepared from Iraqi rice husk and then impregnated with copper. Investigators were performed adsorption/breakthrough experiments in vertical column made quartz adsorbers equipped with a supporting glass fits. They were used Antek 9000s total sulfur analyzer for sulphur analysis.Authors were demonstrated that Y-zeolite prepared from Iraqi rice husk and impregnated with copper gave good results for the removal of sulfur compounds from simulated diesel fuel, based on dynamic fixed-bed adsorption experiment[12].

Kinetic Study of Diesel Fuel by Batch Adsorption on Activated Carbon was studied by Neran K. Ibrahim and Samar K. Aljanabi .They were studied a batch adsorption desulfurization process for diesel fuel containing 580ppm sulfur, based on physical adsorption of refractory sulfur compounds on activated carbon .Authors were investigated the 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 .Investigators carried out batchwise experimental runs. They were applied different kinetic models to fit the experimental data and the experimental adsorption isotherms were correlated by Langmuir and Freundlich models .and sulfur content in the treated diesel fuel phase was then measured using x-ray fluorescence sulfur analyzer. Authors also carried out kinetic experiments in order to gain a better understanding of the adsorption process and evaluate the applicability of activated carbon for the adsorptive desulfurization of diesel fuel. They were also used various kinetic models were used to test the experimental data. Pseudo-first order, pseudo-second order and intraparticle diffusion models were used for this purpose under the assumptions that the organosulfur components in diesel fuel, due to their very low

individual concentrations, can be represented by sulfur concentration as a single component and measured sulfur concentrations are equal to surface concentrations the equilibrium adsorption amount is dependent on the initial sulfur concentration [13].

3. Conclusions

Present study provides various low cost activated carbons which are used as an adsorbent in desulphurization of liquid fuels, as activated carbon has highest adsorption capacity. And it is promising adsorbent for desulphurization. Various investigators carried out adsorption experiments using different low cost adsorbents such as activated carbon prepared from low cost materials such as neem leaves, rice husk, Pd-Impregnated activated carbon, black liquor, clay. It can be concluded that activated carbon is one of the best option for desulphurization of liquid fuels.

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