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Kinetics Analysis and Dosage Effects of Manganese Dioxide Adsorbent on Desulphurization of Crude Oil

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ABSTRACT

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 SO2. Hence, the need for producers to improve their existing technology and to start considering alternative means of isolating sulphur from fuels has become incumbent. Adsorptive desulphurization of crude oil was investigated using activated manganese dioxide, AM in batch reactor. Results showed that desulphurization efficiency was increased on increasing contact time and sorbent dose. There was 49% reduction of crude oil sulphur content after the process. The respective R2 value of pseudo-first order and pseudo-second order reaction model were 0.8162 and 0.9951 when the experimental data were fitted into them. Thus, pseudo-second-order reaction model better described the desulphurization process with chemisorptions being the rate limiting step. However, there is need to improve on methods and adsorbents that will result in complete removal of sulphur from crude oil. Also, the effects of desulphurization on other physico-chemical properties of crude oil should be examined for future research work.

Keyword: Pollutants, combustion, desulphurization, crude oil, kinetic, chemisorption.

INTRODUCTION

The largest and most widely used source of energy in the world is crude oil [1]. However, it contains sulphur (third most abundant element in crude oil after carbon and hydrogen) usually in the form of organic sulphur compounds. Sulphur compounds exist in various forms and can be classified into four main groups: mercaptans, sulphides, disulphides and thiophenes [2]. Figure 1 shows the average composition of crude oils. It is an undesirable component because it forms sulphur dioxide (SO_2) during fuel oil combustion [3]. The combustion of sulphur compounds are not only causing corrosion but also contributing considerably to acid rains and air pollution [4], deforestation, smog, and global warming, as well as several human health concerns such as cardiovascular disease, cancer, creation of asthmatic symptoms and other respiratory diseases [5]. The simplest way to decrease the amount of SO_2 emitted into the air is to reduce the amount of sulphur in fuel [6]. Hence, desulphurization of crude oil is essential to overcome these problems.

At present, oil desulphurization technology can be broadly divided into two categories which are hydrodesulphurization (HDS) and non-HDS (NHDS) [8]. Hydrodesulphurization (HDS) is used to remove sulphur from hydrocarbons in petroleum refineries which require either increasing reactor residence time, or carrying out reactions under higher temperature and pressure [9]. The catalysts used in HDS are not active in removing refractory sulphur compounds like thiophenes and its derivatives. These compounds require higher hydrogen and energy consumption in the HDS process. Non-HDS technology is a reverse case as it does not require higher hydrogen and energy consumption. Adsorption is the most common HDS alternative method currently used to achieve ultra clean fuels [10]. It is often employed to remove trace impurities, such as the removal of trace amounts of aromatics from aliphatics [11] and metal oxides are the adsorbents utilized in petroleum-processing-industries for the desulphurization of crude oil [12].

New Federal regulations require the removal of sulphur in both gasoline and diesel to very low levels, forcing existing technologies to be pushed into inefficient operating regimes [13]. Today, most of the work is concentrated on the application of active metal oxides to form solid metal thiolates [14]. The process is based on thiophenes chemistry in which

metal oxides react with thiophenes to form solid-metal-thiolates. The metal thiolates are insoluble in hydrocarbons and water at sufficiently low temperatures, permitting their removal by filtration [15]. Many new combined technologies for desulphurization of crude oil include hydrogenation-bacterial catalysis method [16], microwave-catalytic hydrogenation method [17], BDS-OD-RA desulphurization process [16], oxidative desulfurization in electrostatic fields [18] and ultrasonic/microwave-catalytic oxidation method [19]. However, many research works on desulphurization of crude oil had been done in the past decades.

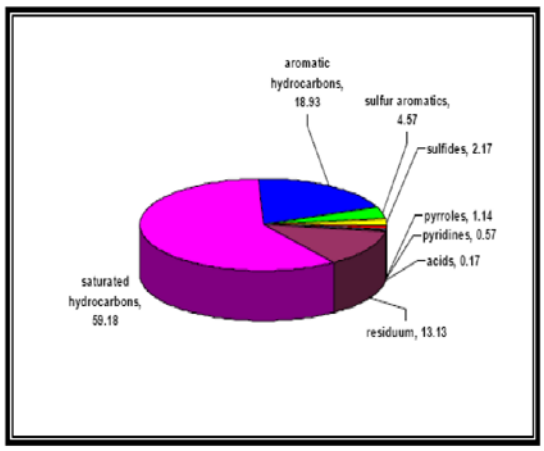

Fig. 1: Average Composition of Crude Oils [7]

Ridley (1969) presented data on desulphurization of fluid petroleum coke with hydrogen, sodium hydroxide and sodium sulphide in which he concluded that the data obtained were consistent with those reported by other investigators of NaOH and NaOH-H_2 systems [20]. Up to 97 percent desulphurization was obtained when processing with the NaOH-H_2 route while up to 74 percent sulphur removal was observed in Na_2S-H_2 system. Rang *et al.* (2006) worked on advances in desulphurization research of liquid fuel in which it was stated that 4-methyldibenzothiophene, 4,6-dimethyldibenzothiophene and their alkyl-substituted derivatives are the key substances that need to be separated from diesel fuel and fuel oil. They observed that these compounds require higher hydrogen consumption in the hydrodesulfurization process and common hydrogenation catalysts are not very effective for their hydrogenization [21]. Zhang *et al.*, (2009) recognized oxidative desulphurization (ODS) technology as one of the most effective methods for the removal of fuel oils, due to the very mild operation conditions it requires. The ODS methods was divided into H_2O_2 oxidation method, organic oxidant method, photochemical oxidation method, as well as those involving the use of plasma or ultrasound based on the oxidants involved [22].

Recently, oxidative desulphurization of jet and diesel fuels using hydroperoxide generated in-situ by catalytic air oxidation had been examined by Sundararaman *et al.* (2010) [6]. Lin *et al.* (2010) did theoretical review on progress in the technology for desulphurization of crude oil [5]. Campos-Martin *et al.* (2011) reviewed the developments in selective removal of organosulphur compounds present in liquid fuels via oxidative desulphurization, including both the chemical oxidation and biodesulphurization [23]. Adeyi *et al.* (2012) did comparative study of desulphurization potentials of two metal oxides-activated manganese dioxide and activated zinc oxide, including the kinetic and equilibrium analysis of the adsorption process. The analysis of residual sulphur indicated that significant sulphur depletion occurred with activated manganese dioxide in the five-hour and six-hour reaction times [1]. The ability of the immobilized spores of *Aspergillus flavus* cultured in increasing concentrations of sodium metabisulphite to remove sulphur from crude oil was investigated by Adegunlola *et al.* (2012) [24]. Hammad *et al.* (2012) examined in-situ electrochemical desulphurization of crude oil and its fraction [25]. Sundararaman *et al.* (2013) investigated oxidative desulphurization of crude oil incorporating sulphone decomposition by alkaline earth metal oxides. They explored a novel approach to desulphurization of whole crude oil where thiophenic sulphur compounds were oxidized to sulphones followed by sulphone decomposition into sulphur-free hydrocarbons [26].

Scope of Study

In batched experiments, manganese dioxide was applied to adsorb sulphur in the crude oil. This research work explored the influence of contact time and doses of adsorbent. X-Ray Fluorescence spectrophotometer was used to determine the remaining sulphur in each sample after adsorption. The kinetics analysis of sulphur uptake from crude oil sample was executed using pseudo-first-order and second-order rate equations.

MATERIALS AND METHODS

Adsorbent*:* Manganese dioxide (MnO_2) used was 98.95 % pure, 1.7 mm particle size, 5.026 g/cm^3 density and products of M and B laboratory chemicals, England. Its adsorptive capacities was increased by oven drying at 110 ^{0}C for 4.00 hours, and then stored in desiccators.

Crude oil: The crude oil used in this research was Escravos obtained from Kaduna Refining and Petrochemical Company (KRPC), Kaduna, Nigeria.

Desulphurization Experiment: Batch adsorptive desulphurization experiments were performed by contacting 2 g of the adsorbent-Activated manganese dioxide (MnO_2) powder with 20 ml of crude oil. The experiment was performed on magnetic stirrer (model A-034) for a period of 1 hour at 120 rpm using 250 ml flask containing 20 ml of crude oil sample and 2 g of adsorbent at room temperature (30 ^{0}C). Continuous mixing was provided during the experiment by agitating at constant speed (120 rpm) for better mass transfer with high interfacial area contact. The remaining sulphur in each sample after adsorption at different time intervals (60, 120, 180, 240, 300 and 360 minutes) was determined by X-Ray Fluorescence spectrophotometer (SULPHUR-IN-OIL ANALYZER) shown in figure 2 using ASTM (D-2622) method. This was done by placing the filtered sample in an X-ray beam and intensity of the sulphur X-ray fluorescence was measured.

Fig. 2: X-ray Fluorescence Spectrometer (SULPHUR-IN-OIL ANALYZER)

The quantity of sulphur retained in the adsorbent phase was calculated using (1) [27]:

$$q_t = \frac{(C_o - C_t)\,V}{W} \quad (1)$$

Where q_t = Quantity of adsorbed sulphur on adsorbent surface, mg g^{-1},
C_o = Initial concentration of sulphur solution, mg kg^{-1},
C_t = Final concentration of sulphur solution, mg kg^{-1},
V = Volume, ml,
W = Mass of the adsorbent, g.

The percentage sulphur removal was estimated using (2):

$$\%Desulphurization = \frac{(C_o - C_t)}{C_o} \times 100 \quad (2)$$

Kinetic Study: The kinetics of adsorption was determined by analyzing adsorptive uptake of sulphur from the crude oil sample at different time intervals. The pseudo-first-order (3) and pseudo-second order (4) model equations were fitted to model the kinetics of sulphur adsorption onto activated manganese dioxide (AM). The linearity of each model when plotted indicates whether the model appropriately described the desulphurization process or not. The pseudo-first-order model equation is given as:

$$\ln\,(q_e - q_t) = \ln q_t - k_{s1}\,t \quad (3)$$

Where q_e = Balance adsorption capacity, mg g^{-1},
q_t = Quantity of adsorbed sulphur on adsorbent surface, mg g^{-1},
K_{s1} = Adsorption rate constant of pseudo first-order kinetic model, min^{-1},
t = Time, min.

The pseudo-second order model equation is stated as:

$$\frac{t}{q_t} = \frac{1}{k_{s2}\,q_e^2} + \frac{1}{q_e}\,t \quad (4)$$

Where K_{s2}- adsorption rate constant of pseudo-second-order, g mg^{-1}, min^{-1}. Other terms remain as stated in (3).

These models were used with the premise that the adsorption of organic sulphur compounds from crude oil due to its low concentration could be observed as the adsorption of one component represented by sulphur content in fuel with high selectivity of these adsorbents towards sulphur [28, 29].

RESULTS AND DISCUSSION

Characterization of Crude Oil Sample: The result obtained for the characterization of the crude oil used in this study before and after desulphurization to determine the sulphur content is stated in table I.

Table I: Characterization of the Crude Oil Sample before and after Desulphurization

Property	Sample before desulphurization	Sample after desulphurization	ASTM Standard
Sulphur content (wt %)	0.16443	0.08386	0.05-6.0
Flash point (^{0}C)	43.52	-	40 - 48
Viscosity (cSt)	4.32	-	4.0 - 6.0
Salt (wt %)	3.00	-	2.90 - 4.10
Base sediment & water (wt %)	0.10	-	0.1 - 0.3
API gravity	36.0	-	15 - 40
Specific gravity	0.8456	-	0.8 - 1.0058

The result presented in table I indicate that there is reduction in the sulphur content of the examined crude oil after desulphurization by 49%. The sulphur content reduces from 0.16443 wt% to 0.08386 wt%. Both values fall within the range of the recommended ASTM standard of 0.05 – 6.0 wt% before and after the experiment. This is an indication that the sampled crude is ASTM standardized. Also, the adsorbent (activated manganese dioxide) used proved to be efficient for the desulphurization of the crude oil. Previous literatures had shown that activated manganese dioxide is a better adsorbent than activated zinc oxide and some other metallic oxides for desulphurization of crude oil [1, 5]. Though other properties of the crude oil after its desulphurization was not check, they fall within the range of ASTM standard when examined before the experiment as shown in table I. These include the flash point; viscosity; salt content; base sediment and water content; API gravity and specific gravity.

The Effect of Adsorbent Dose on Desulphurized Crude Oil: Dosage of adsorbent is a key parameter to control both availability and accessibility of adsorption sites [30].The effect of adsorbent dose was studied at room temperature (30 ^{0}C) by varying the sorbent amounts from 1 g to 5 g, with an initial

sulphur concentration of 0.16443 mg/kg. Result obtained on the effects of adsorbent dose on the quantity of sulphur removal is as presented in figure 3.

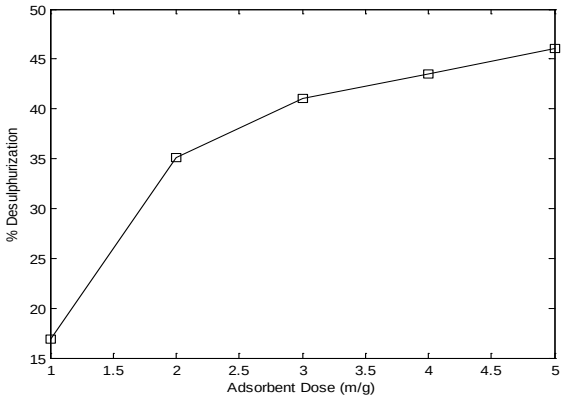

Fig. 3: Effect of adsorbent dose on desulphurization

Figure 3 shows that the adsorption of sulphur increases rapidly with increase in the amount of activated manganese dioxide (AM) due to greater availability of the surface area at higher concentration of the adsorbent. The significant increase in uptake was observed when the dose was increased from 1 g to 4 g. Any further addition of the adsorbent beyond this did cause little change in the adsorption. This may be due to overlapping of adsorption sites as a result of overcrowding of the adsorbent particles [31]. From this result, it was revealed that the percentage of sulphur adsorption on AM was determined by the sorption capacity of the adsorbent. The maximum removal of sulphur was obtained at 4 g dosage of adsorbent.

The Effect of Contact Time: Adsorption of sulphur was measured at constant sulphur concentration for six different contact times from 1 to 6 hours at room temperature and fixed amount of AM. The result obtained is presented in figure 4 below.

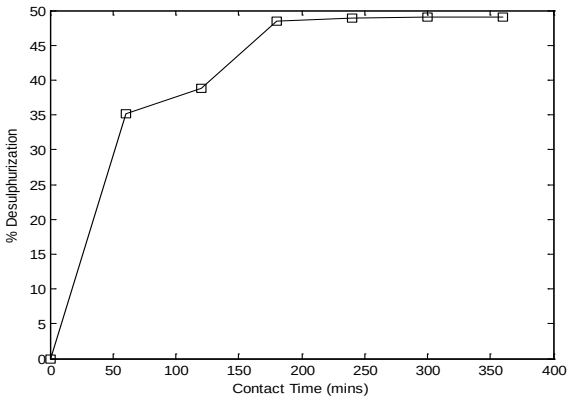

Fig. 4: Effect of contact time on desulphurization

Figure 2 reveals that the rate of sulphur removal is higher at the beginning. This is probably due to the availability of large surface area of the adsorbent being available at the beginning for the adsorption of sulphur. The maximum percent desulphurization was attained after about 300 minutes of contact time. The increasing contact time result to increase in the sulphur sorption. This observation was also reported [32, 33]. The contact-time experimental results can be used to study the rate-limiting step in the adsorption process, as suggested by [34].

Adsorption Kinetics (Dynamics): Adsorption is a mass transfer process involving transfer of adsorbate from liquid phase into solid phase, and it includes 3 steps: (i) Boundary layer mass transfer across the liquid film around the particle, (ii) Internal diffusion /mass transport within the particle boundary as pore and /or solid diffusion, (iii) Adsorption within the particle and or on the external surface [35, 36]. The data obtained on dependence of adsorption capacity with time were used for kinetic analysis. Figures 5 and 6 respectively show the tests of pseudo-first-order rate equation and pseudo-second-order rate equation.

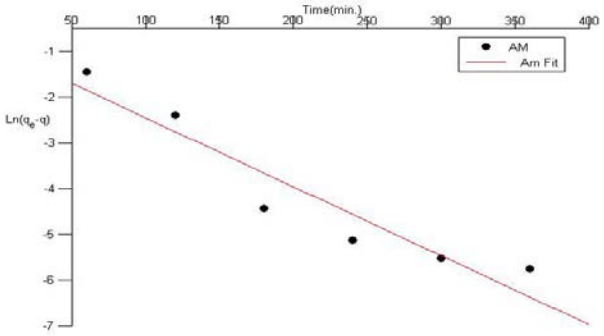

Fig. 5: Pseudo-first-order reaction model

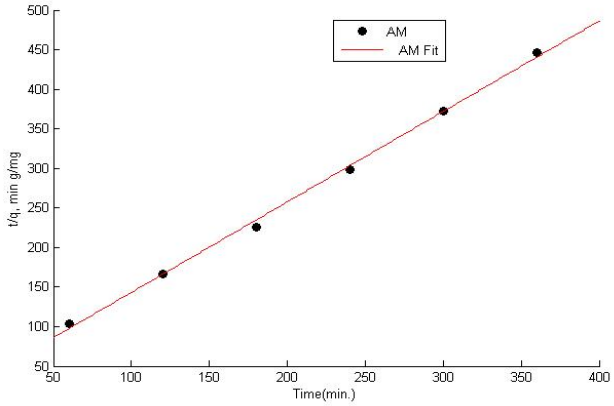

Fig. 6: Pseudo-second-order reaction model

The kinetic analysis for both pseudo-first order model and pseudo-second order model was done

in such a way that balance adsorption capacity, $q_{e,}$ of the used adsorbents included the values measured after 400 min (0.8100 mg g^{-1}). It was assumed that the equilibrium of the system had been reached under this condition. From the results of the fitting of the data to the various models, the respective R^2 value of pseudo-first order and pseudo-second order reaction model were 0.8162 and 0.9951. This shows that pseudo-second-order reaction model described the data better due to the closeness of its correlation coefficient value to 1 and closeness of the values of equilibrium adsorption capacity (q_e) to the estimated capacity values after 400 min. These established facts suggest that the adsorption of sulphur compounds by activated manganese oxide powder follows the pseudo-second-order kinetic model, which relies on the assumption that

chemisorption may be the rate-limiting step. In chemisorption, the sulphur sticks to the adsorbent surface by forming a chemical bond and tend to find sites that maximize coordination number with the surface [37]. Thus the sorption of sulphur can be said to follow a pseudo-second order model, with chemical sorption as its rate limiting step.

CONCLUSION

The kinetics analysis and dosage effects of manganese dioxide adsorbent on desulphurization of crude oil had been examined. The activated manganese dioxide proved to be efficient during the adsorption of sulphur compounds from crude oil. Pseudo-second order kinetic model fits better into the experimental data obtained. Thus, sorption of sulphur can be said to follow a pseudo-second order model, with chemical sorption as its rate limiting step. Also, desulphurization efficiency was found to increase with increasing sorbent dose and contact time. There was reduction in the sulphur content of the examined crude oil by 49 % after desulphurization. However, there is need to improve on methods and adsorbents that will result in total removal of sulphur from crude oil. Also, the effects of desulphurization on other physico-chemical properties of crude oil should be examined for future research work.

Nomenclature:

C_e – balance sulphur content in crude oil, $mgkg^{-1}$,
C_0 – initial sulphur concentration, mg kg^{-1},
C_t – sulphur content in crude oil at specified time, mg kg^{-1},
K_{s1} --adsorption rate constant of pseudo first-order kinetic model, min^{-1},
K_{s2}- adsorption rate constant of pseudo-second-order, g mg^{-1}, min^{-1},
W – Mass of adsorbent, g,
q_m – maximum adsorption capacity, mg g^{-1},
q_t –quantity of adsorbed sulphur on adsorbent surface, mg g^{-1},
q_e –balance adsorption capacity, mg g^{-1},
t – Time, min.

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