Comparative Analysis of Adsorptive Desulphurization of Crude Oil by Manganese Dioxide and Zinc Oxide

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Abstract

Desulphurization of crude oil has lately become one of the most important processes in crude oil refining. Increasingly stringent environmental protection regulations mean that motor fuel producers must improve their existing technology and to start considering alternative means of isolating sulphur from crude oil. Adsorption is a process that can be applied for crude oil desulphurization. The idea is to selectively separate less than 1 wt.% of fuel mass by selective adsorption for removing sulphur, and leave the 99 wt.% of non sulphur-containing crude oil mass untouched. A comparative study was made of the desulphurization potentials of two metal oxides-activated manganese dioxide, AM and activated zinc oxide, AZ. Kinetic and equilibrium analysis of the adsorption process was done. The analysis of residual sulphur indicated that significant sulphur depletion occurred with activated manganese dioxide in the five-hour and six-hour reaction times. Kinetic analysis was best described by pseudo-second-order model. Both Langmuir and Freundlich models were well fitted for the balance analysis of the adsorptive desulphurization.

Keywords: Comparative, adsorptive, desulphurization, kinetic, crude oil.

Introduction

Crude oil is the largest and most widely used source of energy in the world. Major portions of the crude oils are used as transportation fuels such as gasoline, kerosene (jet fuel) and diesel. However, such crude contain sulphur, typically in the form of organic sulphur compounds. The predominant modern technique for fossil fuels refining has a severe impact on the global environment. Some of this impact is the result of impure fuels. Sulphur is the third most abundant element after carbon and hydrogen in fossil fuel. Sulphur compounds exist in various forms and can be classified into four main groups: mercaptans, sulphides, disulphides and thiophenes. It is an undesirable component because it forms sulphur dioxide (SO_2) during fuel oil combustion[1].

The combustion of sulphur compounds are not only causing corrosion but also contributing considerably to acid rains and air pollution[2], 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. Sulphur compounds also deactivate some catalysts used in crude oil processing. Sulphur compounds can cause several corrosion problems in pipeline, pumping, and refining equipment, as well as the premature failure of combustion engines and poisoning of the catalytic converters that are used in automotive engines. Today, the strongest motivation for the reduction of sulphur in fuels is due to environmental protection agency's regulation which is imposing stringent limits for sulphur levels in transportation fuels.

Desulphurization prior to combustion has been viewed in recent years with the objective of ensuring clean fuel combustion and hence to avoid environmental degradation. There are three major approaches recognized for controlling sulphur oxides pollution. The first is to use fuels of naturally low sulphur content. The second approach is the desulphurization of the fuel, which in the case of oil is usually accomplished by hydrogen processing. The third method is the removal of sulphur compounds from stack gases primarily from large combustion operation such as power generator[3]. Therefore, desulphurization of oil is extremely important in the petroleum-refining company[4].

Conventional hydrodesulphurization (HDS) is currently being used in the petroleum industry. HDS is the only one widely used industrial technology, which has a number of shortcomings: application of complicated equipment, purified hydrogen which is of short supply and expensive, very high energy operating conditions (high temperature and pressure) and removal of heteroatomic products and a part of aromatic hydrocarbons together with sulphuric compounds. All above-mentioned shortcomings require the development of new method of fuel desulphurization that is non-hydrogen consuming because HDS process is not only too expensive in terms of costly hydrogen but also too tedious[5]. HDS also has limited effectiveness at removing thiophenes, benzothiophene, dibenzothiophene and it's derivatives from crude oil[6].

Therefore, there is a need to research new desulphurization methods which are cost effective, more efficient and can meet the environmental regulations and refining requirements. Much effort has been devoted to developing techniques that can reduce or remove such refractory sulphur compounds by oxidation[7], extraction8, adsorption[9] and biodesulphurization[10].

Adsorption is the most common HDS alternative method currently used to achieve ultra clean fuels[11]. Adsorption is a mass transfer process wherein molecules in a free phase become bound to a surface by intermolecular forces[12]. It is often employed to remove trace impurities, such as the removal of trace amounts of aromatics from aliphatic[13].

Metal oxides are highly reactive towards sulphur compounds, especially thiols. 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. The metal oxide can also be recovered by decomposing the thiolate with an oxidizing acid. The process works with any combination of metal oxides and thiophenes form stable insoluble compound. Numerous oxides and hydroxides of Na, Pb, Hg (II) and Ba have been found to react efficiently with thiophenes[15].

In the present study, metal oxides will be applied to capture sulphur in crude oil. The study will explore the possibility of developing means of forming metals-sulphur-organic compounds complex for sulphur removal without using hydrogen at lower operation conditions. Such a method would offers a very cost effective route if proven to be successful.

Material and Methods

Adsorbent: The adsorbents used were 98.95% pure manganese dioxide (MnO_2) and 99.00% pure zinc oxide (ZnO), all products of M and B laboratory chemicals, England. Their adsorptive capacities were increased by oven drying at 110^0C for 4 hours and then stored in desiccators.

Crude oil: Four samples of crude oil with different sulphur content were tested. Their respective properties are listed in table 1.

Table-1
Properties of samples of crude oil

Property	Sample A	Sample B	Sample C	Sample D
Specific gravity	0.8456	0.8022	0.8360	0.85621
Flash point (^{0}C)	43.52	42.18	43.40	44.10
Viscosity	4.32	4.30	4.51	4.35
Salt (wt %)	3.00	3.10	2.90	3.20
Base sediment and water (wt %)	0.10	0.10	0.10	0.10
API gravity	36.00	36.75	37.00	36.00
Sulphur content (wt %)	0.16443	0.23842	0.29116	0.34810

Batch adsorptive desulphurization experiments were performed by contacting 2 g of the adsorbent-activated manganese dioxide (MnO_2), AM powder with 20 ml of crude oil in 250 ml flask and stirred with a magnetic stirrer for a period of 60 minutes at 120 rpm and at a temperature of 30^0C. Similar experiments were performed at 120, 180, 240, 300 and 360 minutes respectively. The sulphur content of each sample was analysed by means of X-Ray Fluorescence spectrophotometer (Sulphur-in-oil analyzer) after filtering out the adsorbent with Whatman filter paper number 42.

The above experimental procedure was also followed in the case of second adsorbent- Activated zinc oxide, AZ.

The sulphur concentration retained in the adsorbent phase was obtained from equation (1):

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

Where C_o and C_t are initial and equilibrium concentrations of sulphur solution respectively: V is the volume (ml): and W is the mass (g) of the adsorbent.

The percentage sulphur removal was obtained from equation (2):

$$q_t = \frac{(C_o - C_t)\, V}{W} \qquad (2)$$

The balance of adsorption was determined by analysing adsorptive uptake of sulphur from crude samples at constant time. The adsorption isotherm was obtained from the results of agitating the solution with different initial sulphur concentration and 2 g of adsorbent till equilibrium was achieved. For these experiments, the mixture was agitated at a speed of 120 rpm for a minimum contact time of 60 minutes.

Kinetic Analysis: The experimental kinetic data obtained were treated with four models, namely: First-order kinetic model, pseudo-first-order kinetic model, second-order kinetic model and Pseudo-second-order models represented by equations (3) to (6) respectively:

$$\ln C_t = \ln C_o - k_1 t \qquad (3)$$
$$\ln (q_e - q_t) = \ln q_t - k_{s1} t \qquad (4)$$
$$\frac{1}{C_t} = \frac{1}{C_o} + k_2 t \qquad (5)$$
$$\frac{t}{q_t} = \frac{1}{k_{s2} q_e^2} + \frac{1}{q_e} t \qquad (6)$$

In testing these models, the adsorption of organic sulphur compounds from crude oil at low concentration can be considered as the adsorption of one component represented by sulphur content in crude oil. This is because the adsorbents are highly selective for sulphur. A certain number of authors have successfully used this premise in similar studies[16-18].

Equilibrium Analysis: Equilibrium analysis of adsorptive desulphurization of crude oil was carried out by using linearized Langmuir and Freundlich models represented by equations (7) and (8) respectively[19, 20]:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \qquad (7)$$

$$\ln(q) = \ln k_f + \frac{1}{n} \ln(C_e) \qquad (8)$$

Results and Discussion

Kinetic Analysis: The result of sulphur uptake which is a measure of the adsorption capacity with time for 2 g adsorbent is illustrated in figure 1. From the figure, it is clear that activated manganese dioxide (AM) has higher adsorptive capacity than activated zinc oxide (AZ) for the time range considered.

Figures 2 to 5 show the tests of first-order reaction, pseudo-first-order rate equation [Lagergren Model], second-order reaction and pseudo-second-order rate equation [Ho Model] respectively:

From the results of the fitting of the data to the various models, it is clear that pseudo-second-order reaction model best describe the data. The estimation via Lagergren model was conducted in a way that the left side of equation (4) as balance adsorption capacity, q_e, of the used adsorbents included the values measured after 400 min (AM: 0.8100 mg g^{-1}, AZ: 0.5152 mg g^{-1}), when it was assumed that the equilibrium of the system was reached. The values of balance adsorption capacity calculated via Lagergren model significantly scattered (non linear) and differ from the adsorption values measured after 400 minutes which confirms the inadequacy of the model for the process.

Both facts suggest that the adsorption of sulphur compounds by activated metal oxides 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 stick to the adsorbent surface by forming a chemical

(usually covalent) bond and tend to find sites that maximize their coordination number with the surface.

The excellence of pseudo-second-order (Ho model) for describing the kinetics of adsorptive desulphurization of crude oil was confirmed by closeness of the values of equilibrium adsorption capacity (AM: 0.8162 mg g^{-1}, AZ: 0.5274 mg g^{-1}) to the estimated capacity values after 400 min where the values of correlation coefficients reach values almost equal to 1, (AM: 0.9951 mg g^{-1}, AZ: 0.9903 mg g^{-1}), while the corresponding R^2 values of first-order, pseudo-first-order and second-order reaction models cannot be calculated (because of non-linearity) which once again, proves that these models are not adequate for describing this process.

Equilibrium Analysis: Equilibrium analysis was carried out based on the data of the dependence of adsorption capacity to initial sulphur concentration which is shown in figure 6. These isotherms show that the research of balance characterization gave the better results when activated manganese dioxide was used.

Figures 7 and 8 respectively show the results of the fitting of Langmuir and Freundlich models to the sulphur uptake data. The results clearly show a good fit of the data by both models. The model adsorption parameters and the correlation coefficients are shown in table 3. However, the best model for activated manganese dioxide was Langmuir model whereas that of activated zinc oxide was the Freundlich model.
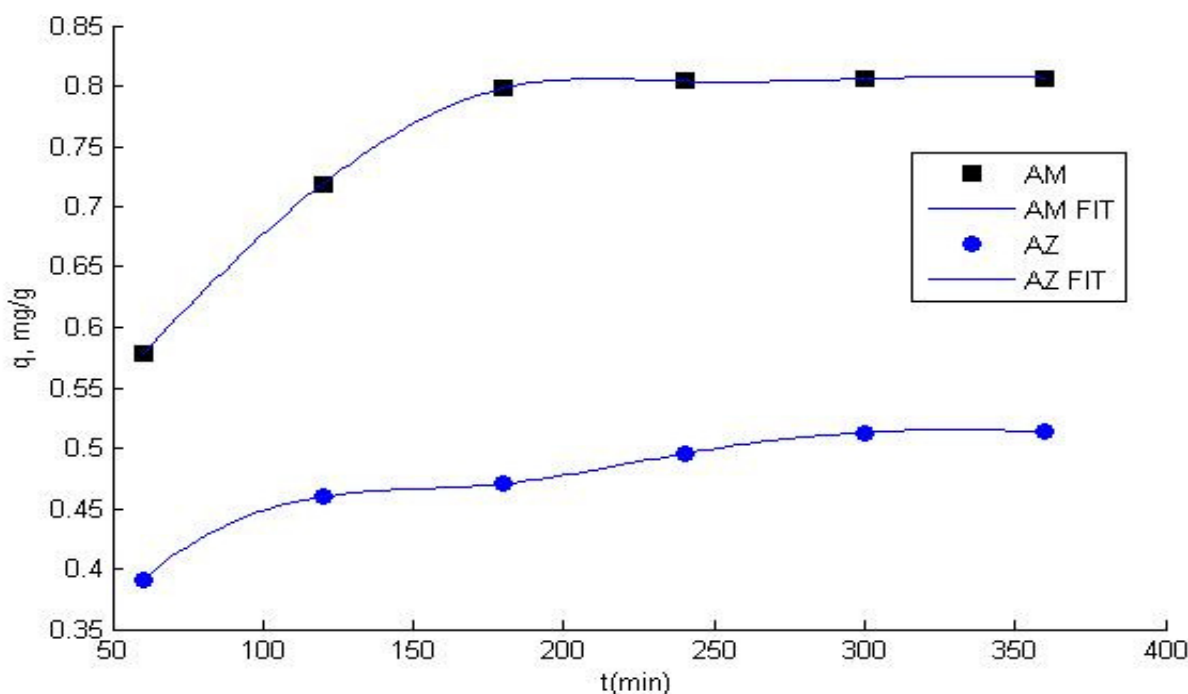

Figure-1
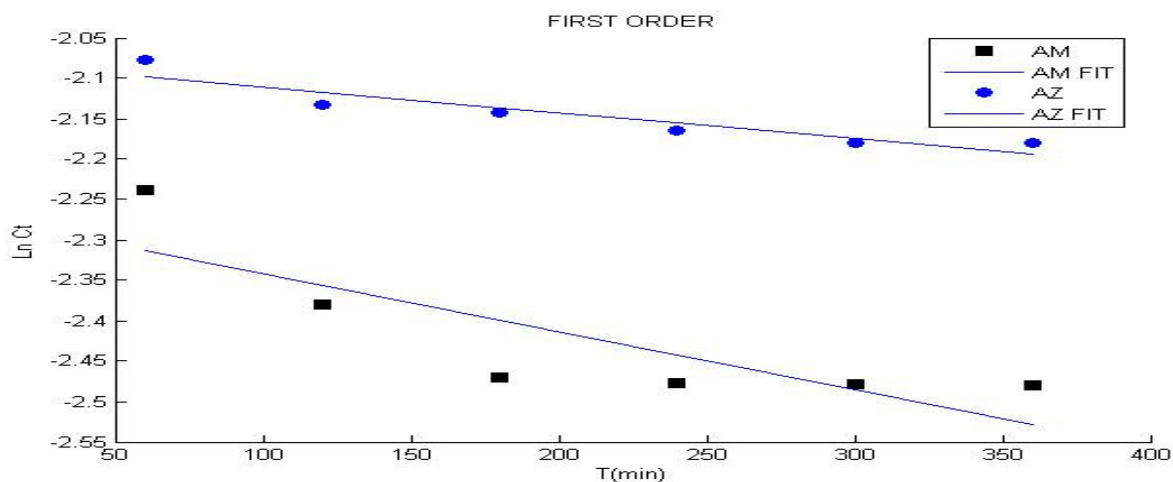**Dependence of adsorption capacity on time for tested adsorbents (T = 30⁰C, m = 2.00 g)**

Figure-2
First-order reaction model
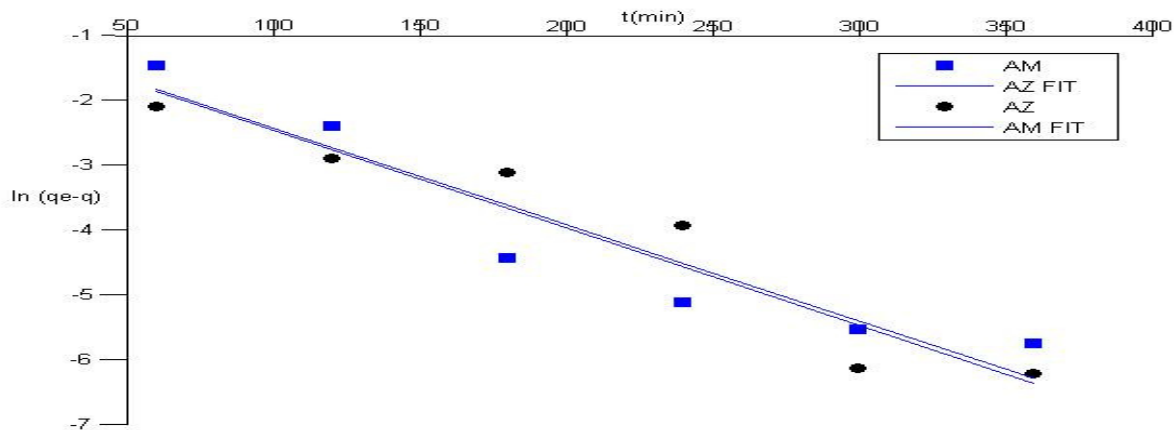

Figure-3
Pseudo-first-order reaction model
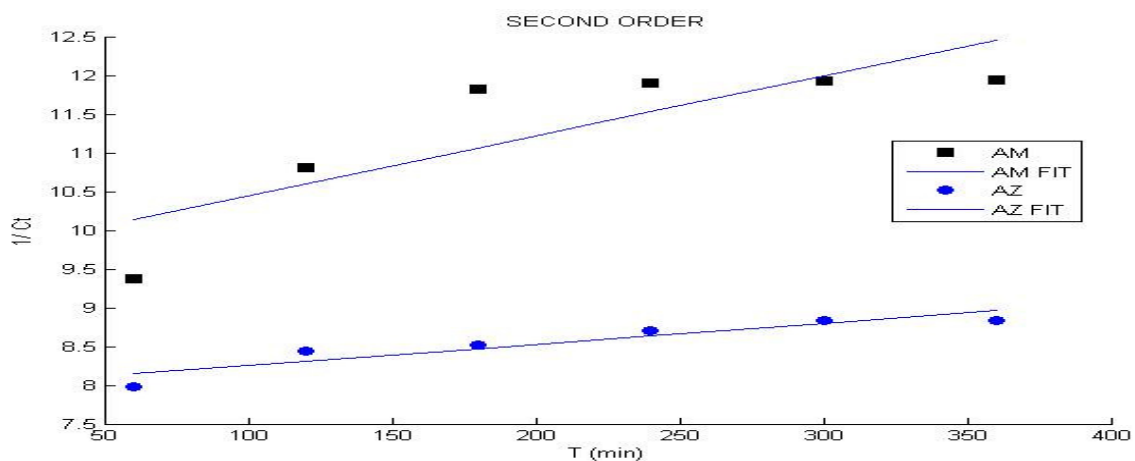

Figure-4
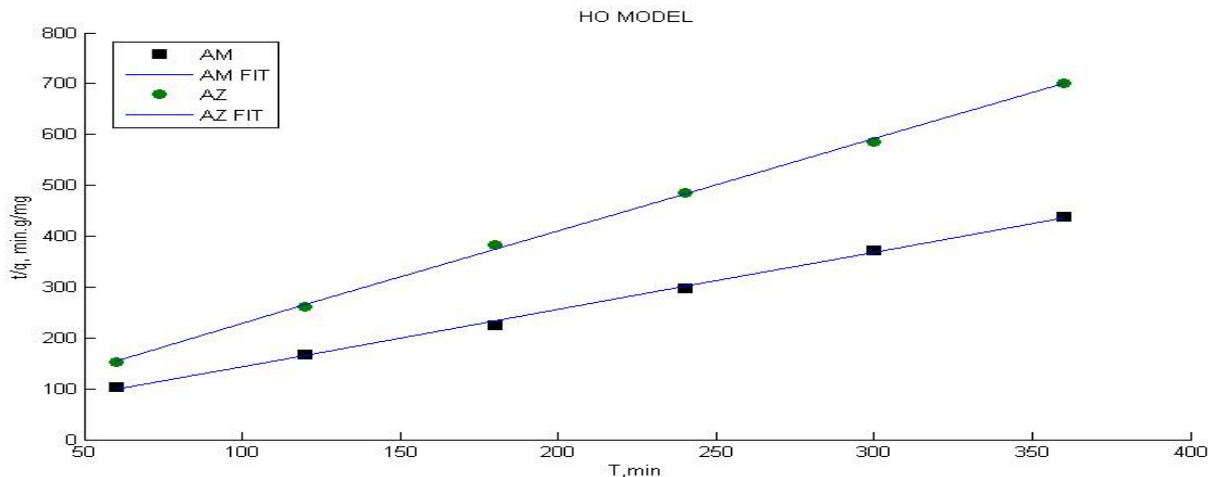**Second-order reaction model**

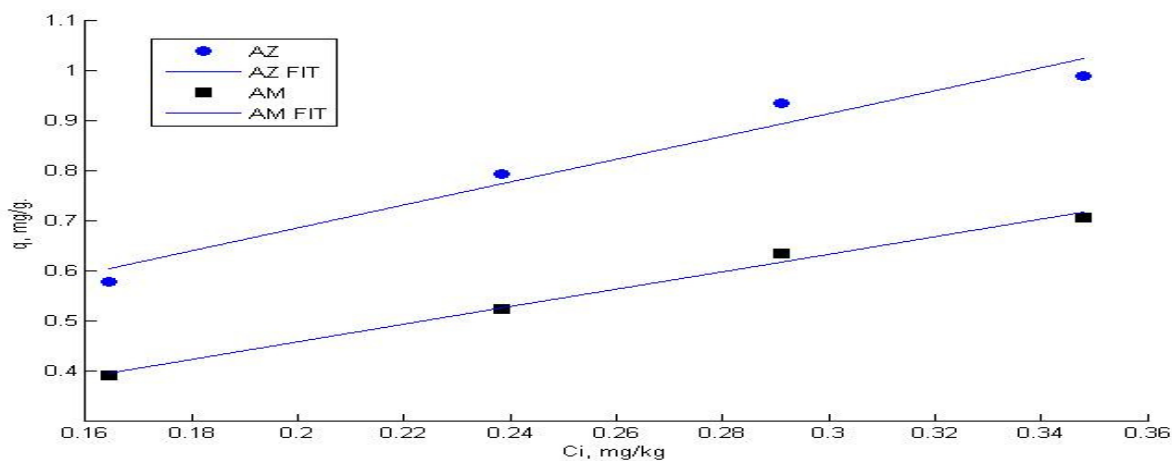**Figure-5**
Pseudo-second-order reaction model

Figure-6
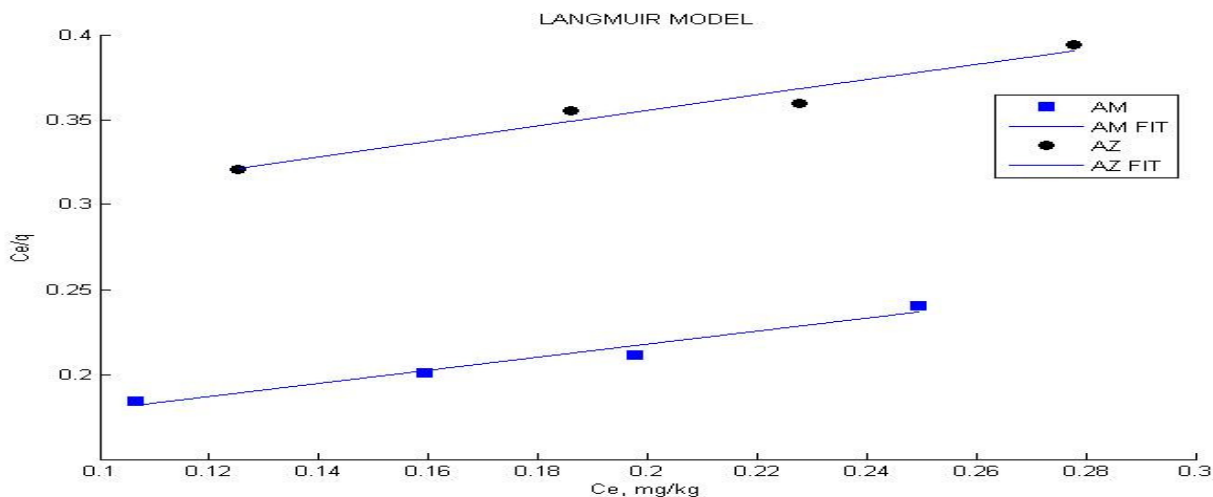**Adsorption isotherms for tested adsorbents**

Figure-7
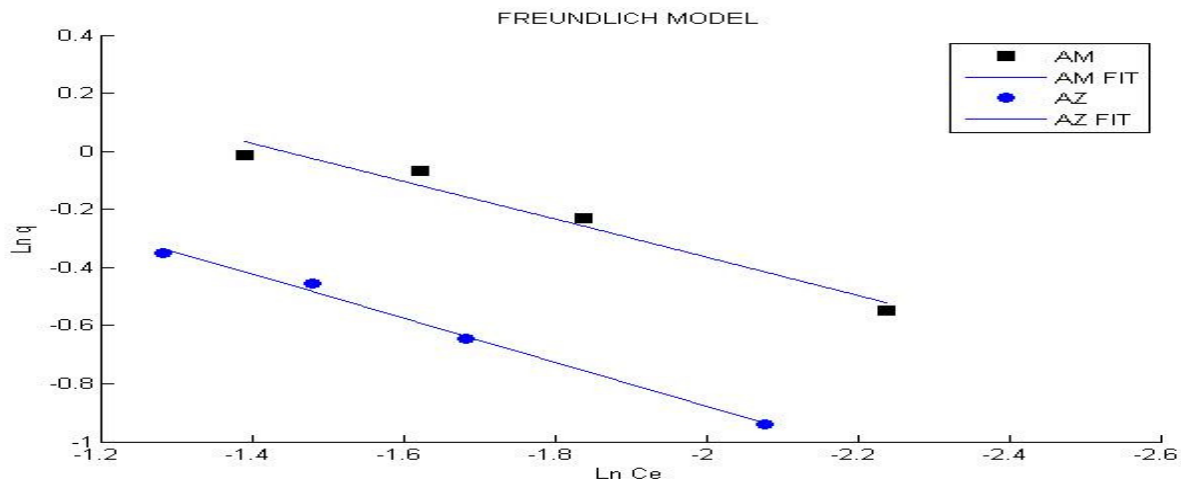**Langmuir adsorption isotherms**

Figure-8
Freundlich adsorption isotherms

Table-2
Constants of Langmuir and Freundlich models and correlation coefficients

Models	AM	AZ
Langmuir K_L**, kg mg**$^{-1}$	0.4123	0.6909
q_m, mg g^{-1}	0.5484	0.2258
R^2	0.9700	0.9550
Freundlich K_f	2.5702	1.8908
n	1.5291	1.3193
R^2	0.9650	0.9940

Conclusion

The comparative analysis of removing sulphur from crude oil was tested using the process of adsorption. The adsorption was conducted on activated manganese dioxide, AM and activated zinc oxide, AZ. Activated manganese dioxide proved to be more efficient during the adsorption of sulphur compounds from crude oil when compared to activated zinc oxide. The kinetic research, in the cases of both used adsorbents established that experimental and calculated data coincide better when pseudo-second-order model (Ho model) is being used. The balance characterization for both used adsorbents showed that the process of adsorption desulphurization is better described both by Freundlich model and Langmuir model and here physical adsorption was the case. However, the best model for activated manganese dioxide was Langmuir model whereas that of activated zinc oxide was the Freundlich model.

During kinetic and balance research better results are gained for the use of activated manganese dioxide, AM.

Acknowledgement

Nomenclature: C_e – balance sulphur content in crude oil, mg kg^{-1}, C_0 – initial sulphur concentration, mg kg^{-1}, C_t – sulphur content in crude oil at specified time, mg kg^{-1}, K_f– Freundlich constant related to adsorption capacity, mg g^{-1}, K_L – Langmuir constant, g mg^{-1}, K_1 – adsorption rate constant of first-order kinetic model, min^{-1}, K_{s1}– adsorption rate constant of pseudo-first-order kinetic model, min^{-1}, K_2 – adsorption rate constant of second-order kinetic model mg^{-1} min^{-1}, K_{s2}- adsorption rate constant of pseudo-second-order, g mg^{-1}, min^{-1}, W – Mass of adsorbent, g, n – Freundlich constant related to adsorption intensity, 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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