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OPERATING PARAMETERS EFFECT ON ADSORPTIVE DESULPHURISATION PROCESS OF DIESEL OIL

Md Firoz Kalam, Wilfried Schütz*
University of Applied Sciences Bremerhaven, An der Karlstadt 8, 27568 Bremerhaven, Germany, Department of Process Engineering and Energy Technology,
e-mail: wschuetz@hs-bremerhaven.de
* Corresponding author

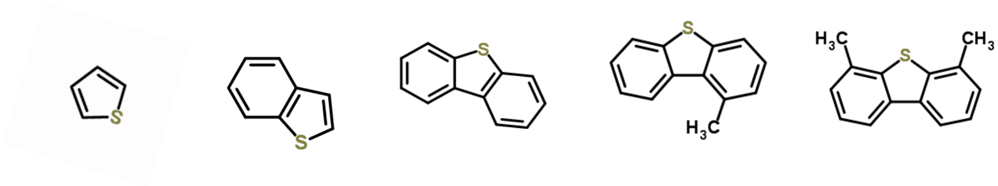
Abstract: The vision of this research was to investigate the removal of thiophene sulphur compounds from high sulphur content (1.3%) diesel oil by adsorptive desulphurisation process using powdered activated carbon. The adsorptive desulphurisation process was performed under three different operating conditions such as amounts of activated carbon (g), treatment temperatures (°C) and stirring time (minutes). Results showed that these operating parameters influence the removal of sulphur compounds from diesel oil. The maximum desulphurisation obtained was 76.16%.

Keywords: Desulphurisation, Diesel Oil, Adsorption, Activated Carbon (AC).

1. INTRODUCTION

Production of diesel oil with low sulphur and aromatic content has become one of the most challenging tasks for refineries. High contents of sulphur compounds or impurities are not only a hindrance in refining operations, but also poisoning the catalyst in further processes [Gang et al. 2011] and finally the environment. High sulphur concentrations and aromatic contents oil enhance the exhaust emissions produced from the diesel oil engine during the combustion. These emissions from diesel engines are the principle causes of environmental degradation and cause global warming and acid rain [Stanislaus, Marafi and Rana 2010]. With the intention of protecting the environment from contaminations, legislative authorities and scientific communities from many countries have attributed new regulations for eliminating sulphur from diesel oil in ultra-low level, so called “Ultra Low Sulphur Diesel (ULSD)” [Kim et al. 2006].

Diesel oil mostly undergoes hydrotreatment but nevertheless contains thiophene sulphur compounds (Fig. 1) due to its high boiling point during crude oil distillation [Javadli and de Klerk 2012]. The reactive nature of thiophene sulphur compounds is relatively low compared to sulphur compounds without benzene ring due to the steric hindrance effect [Ristovski et al. 2006]. As a result, conventional hydrodesulphurisation processes are not able to remove thiophene sulphur compounds selectively, while it eliminates aliphatic sulphur compounds like thiols completely. Several procedures have been introduced and developed in recent years for removing aromatic sulphur compounds.



a) b) c) d) e)

Fig. 1. Chemical structure of: a) thiophene, b) benzothiophene, c) dibenzothiophene, d) 4-MDBT, e) 4,6-DMDBT

Source: [Javadli and de Klerk 2012].

The main purpose of this research is to investigate the adsorption process for eliminating thiophene sulphur compounds from high sulphur content (1.3%) diesel oil using commercial powdered activated carbon (PAC C850 S). The investigation of a batch adsorption process is carried out for different sets of input parameters such as amount of activated carbon, Wac (g), temperature, Topt (°C), and stirring time, t (minute).

2. MATERIALS AND METHODS

The diesel oil (untreated) was collected from Hans Rinck GmbH & Co. KG, which is located in Hamburg, Germany. The sulphur concentration before the treatment was 1.3%. Powdered activated carbon was used as adsorbent for the adsorption. The commercial powdered activated carbon (PAK C 850 S) was supplied by CarboTech AC GmbH from Essen, Germany. UV-visible spectrophotometer was used for measuring sulphur concentration in treated diesel oil due to its simplicity and suitability. The wavelength was considered 265 nm for all treated diesel oil samples.

The desulphurisation efficiency was calculated by following equation

$$\eta(\%) = \frac{S_i - S_f}{S_f} * 100 \quad (1)$$

The adsorption load was calculated by following equation

$$q_e = \frac{(S_i - S_f) * V_{oil}}{W_{ac}} \quad (2)$$

η% – desulphurisation efficiency in percent,
q_e – adsorption load in mg/g,
s_i – initial sulphur concentration in untreated Diesel oil in ppm,
s_f – sulphur concentration in treated Diesel oil in ppm,
V_{oil} – volume of in m^3,
W_{ac} – weight of activated carbon in g.

3. RESULTS AND DISCUSSION

To investigate adsorption kinetic study, it is important to find out the equilibrium contact time. It was developed by experimental work at an operating temperature of 40°C and variation of the contact time from 30 min to 240 min. Other operating conditions such as volume of untreated diesel oil (100 ml), amount of activated carbon (10 g) and initial concentration of sulphur (1.3%) were kept constant.

Figure 2 shows the relationship between, q_e (mg/g) and contact time t in minutes. As seen from Figure 2, adsorption rate qe increases dramatically with increasing contact time up to 30 minutes, while efficiency is increasing rather slowly over the rest period. This may be due to strong intermolecular forces between sulphur atoms in thiophene compounds and the adsorbent surface. It could be also due to high concentration gradient of DBT molecules in the pores of the adsorbent which consequences diffusion resistance by blocking of small pores.

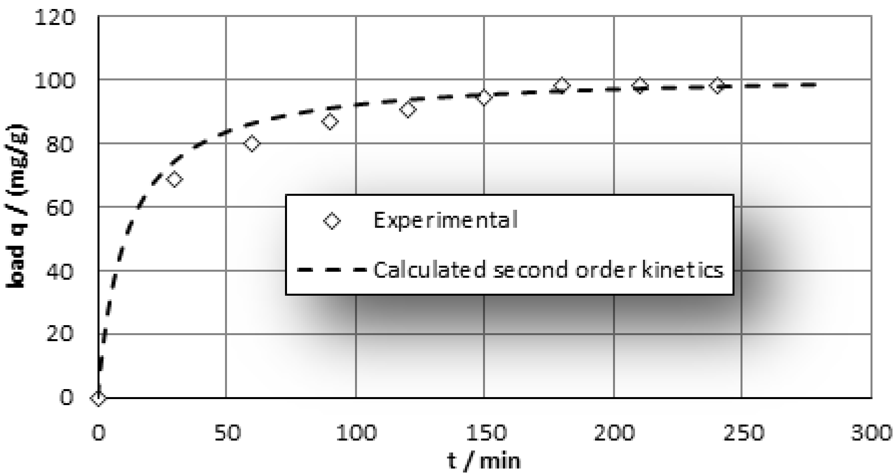


Fig. 2. Effect of stirring time on adsorption load [40°C, 1.3% sulphur, 10 g of AC]

After the initial increase in load there is no notable change of adsorption rate with respect to contact time, q_e reaches almost a constant value which attributes activated carbon is no longer able to absorb sulphur molecules as the active sites of activated carbon are almost filled after dynamic equilibrium is reached at least after 180 min. The adsorption load is 98.2 mg/g after three hours. The time required to reach such a state of equilibrium of sulphur removal indicates the equilibrium sorption capacity. From above discussion it can be drawn that 180 min is the equilibrium time for removal of sulphur compounds from commercial diesel oil (s_i = 1.3%) using activated carbon as adsorbent.

3.1. Effect of Operating Temperature

Operating temperature has definitely an impact on the adsorption process. The diffusion rate increases with increasing temperature while viscosity of the solution decreases. Changing the operating temperature in the system leads to a different sorption capacity. To investigate the effect of temperature on sulphur removal efficiency or desulphurisation efficiency, untreated diesel oil was examined under three different operating temperatures ranging from 20 to 60°C. Other operating conditions such as stirring time of 180 min, a sulphur concentration of 1.3%, an amount of activated carbon of 10 g and a sample volume of diesel oil of 100 ml were kept constant.

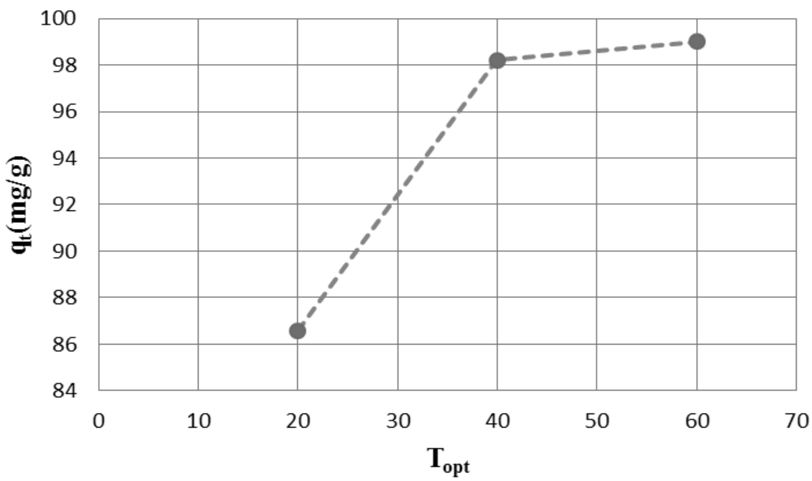


Fig. 3. Effect of operating temperature on adsorption load
[t = 180 min, 1.3% sulphur, 10 g AC]

As seen from Figure 3 and 4, with increasing temperature from 20 to 40°C desulphurisation efficiency is increasing sharply from 67 to 76%, while the adsorption capacity q_e increases from 86.6 to 98.2 mg/g. With increasing temperature sulphur compounds move faster through pores and overcome the activation energy barrier simultaneously. This faster movement of sulphur containing molecules at higher temperatures also attributes the higher concentration gradients at higher temperatures, widening pores of activated carbon and more active site formation on the adsorbent surface due to C-S bond cleavage at higher treatment temperature. However, increasing the operating temperature from 40 to 60°C only leads to slightly higher desulphurisation efficiency, so that the additional amount of sulphur adsorbed on adsorbent surface is small compared to the increase between 20 and 40°C.

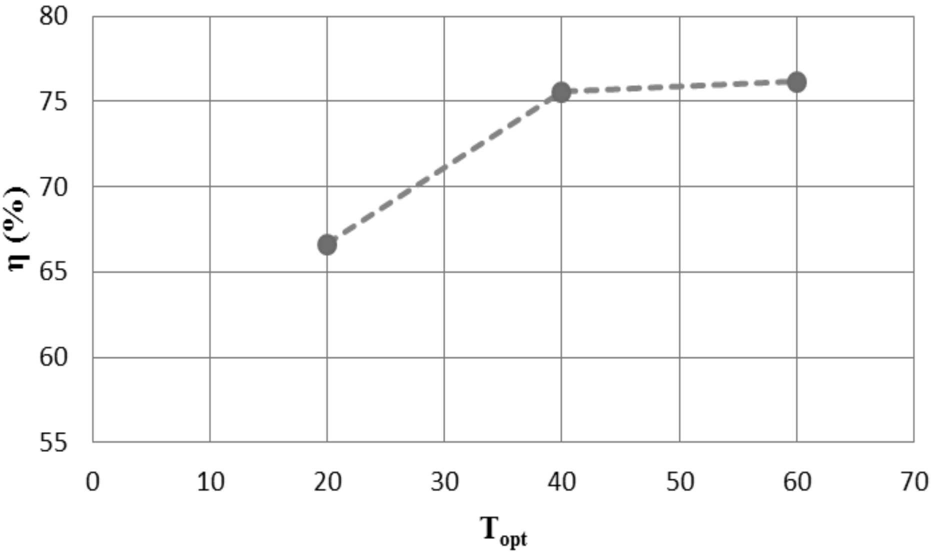


Fig. 4. Effect of operating temperature on desulphurisation efficiency [*t* = 180 min, 1.3% sulphur, 10 g AC]

Even though, in general adsorption capacity decreases with increasing temperature, in this case sulphur compounds are better removed from the oil at 40°C due to lower viscosity and higher diffusion coefficients. It can be concluded that 40°C might be the optimum temperature for removing sulphur compounds (thiophenic) from diesel oil.

3.2. Effect of Amounts of Activated Carbon

With varying amount of adsorbent, the availability and accessibility of adsorption sites can be determined. It was carried out by experimental work at room temperature and varying amount of adsorbent from 3 to 10 g. At the same time, other operating conditions such as volume of untreated diesel oil (100 ml), stirring time of 180 min and the initial concentration of sulphur (1.3%) were kept constant.

Figure 5 shows that desulphurisation increases until stirring with round about 9 g activated carbon. The sulphur removal efficiency is increasing because of the pore volume is also increasing simultaneously. Initially, the availability of surface area of activated carbon is not enough to absorb more sulphur molecules. After adding more activated carbon the surface area as well as the pore volume is increased which enhances the adsorption of sulphur containing molecules on active sites of the carbon. When diesel oil is brought in contact with even higher amounts of activated carbon, the sulphur compound removal efficiencies are not increasing like before. The adsorption happens slowly after adding this amount of activated carbon. This is because of the active sites of activated carbon are mostly filled; hence no vacant sites are available for adsorbing more sulphur molecules on the adsorbent surface.

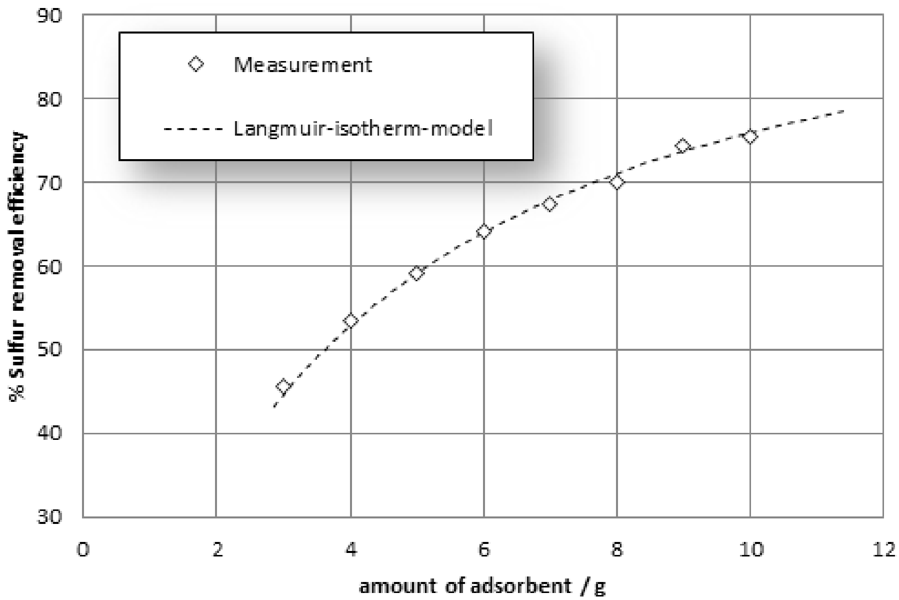


Fig. 5. Effect of quantities of activated carbon on the desulphurisation efficiency [*t* = 180 min, 1.3% sulphur, 10 g AC]

4. CONCLUSION

The batch adsorption process for desulphurisation of diesel oil was performed successfully using commercial powdered activated carbon as an adsorbent. The adsorptive desulphurisation process was performed at different operating conditions. The desulphurisation efficiency was found to be increasing with increasing amount of adsorbents, treatment temperatures and stirring time. The maximum desulphurisation efficiency obtained 76.2% at the best operating conditions of 60°C, 10 g activated carbon and 180 minutes.

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