# Desulfurization of Dibenzothiophene and Thiophene in liquid fuel using Ni-doped carbon beads and a newly isolated bacterial strain

SUMMARY

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# Chapter VIII

## Summary

The purpose of this thesis was to study of desulfurization of DBT and TH using absorptive desulfurization as well as bacterial desulfurization. Additionally, a hybrid strategy was used for complete desulfurization of DBT and TH using both absorption and bacterial desulfurization.

For absorptive desulfurization, the beads were successfully synthesized through suspension polymerization reaction using phenol precursor and formaldehyde solvent. Further, the beads were carbonized, activated and metal nanoparticles present in the beads were then calcined and reduced to obtain nascent forms of the metal nanoparticles. In next, carbon nanofibers were grown onto the surface of the beads through chemical vapour deposition process. The adsorbent was characterized physicochemically using FE-SEM, BET, TPR, XRD, FT-IR, and TGA at different stages of its preparation. Resulting characterization data confirmed successful synthesis of the adsorbent. After synthesis of the adsorbent material, adsorptive desulfurization test was performed for DBT and TH using Ni-ACB and Ni-CNF-ACB adsorbent, respectively. Before the desulfurization test, calibration curves of DBT and TH was plotted using the gas-chromatography analysis. The value of regression coefficient was determined approximately 0.99 indicating the linear relationship between chromatographic area (signal) and concentration of DBT and TH.

Adsorptive desulfurization test was performed at 30 $^{O}$C temperature for four hours in a specially designed reactor. The data showed that approximately 75 – 80 % DBT and TH were adsorbed onto the surface of adsorbent at four different initial concentrations, which were 300 ppm, 600 ppm, 900 ppm, and 1200 ppm. A separate desulfurization test was also performed in respect of time using the same concentrations to know the saturation time of adsorbent. After 2 to 2.5 hours, a saturation was observed in the adsorbent's capacity for adsorption. This may be due to blockage of pores by adsorbed DBT or TH. The adsorbent Ni-ACB was found to be efficient for the adsorption of DBT, but Ni-CNF-ACB was more effective for the adsorption of TH due to TH's affinity toward the carbon material via π-π complexation.

To study the bacterial desulfurization of DBT and TH, *Bacillus zhangzhouensis* strain R-2 or *Enterococcus faecium* strain R5 was used. Desulfurization of DBT and TH was carried out using selected bacteria at 30 $^{O}$C under shaking condition. At the initial concentration of 50-300 ppm, approximately 96-98 % of DBT and TH were removed using bacterial desulfurization.

The adsorptive desulfurization and bacterial desulfurization tests indicate that the adsorptive desulfurization test is effective for high concentrations of DBT and TH. For lower concentrations, bacterial desulfurization is an effective technique. The combination of these two techniques served as an effective method of removing thiol compounds (DBT/TH) from a very high concentration to a low level.

In addition, a complete sequential desulfurization was performed using the prepared adsorbent and the selected bacterial strain. The first time, 99% desulfurization of oils containing DBT and TH was achieved by sequentially applying adsorption at relatively high concentrations, followed by bacterial treatment at low concentrations. The metal nanoparticles-dispersed porous carbon-based beads (Ni-ACB and Ni-CNF-ACB) were used to reduce the sulfur concentration from a high level (300–1200 ppm) to a low level (50 – 300 ppm) via adsorption whereas *Bacillus zhangzhouensis* strain R-2 or *Enterococcus faecium* strain R5 was found to be effective in degrading the remaining S-compounds to ~ 3–15 ppm. Compared with adsorption alone, the hybrid method demonstrated faster desulfurization or higher removal rates. Further, the selected bacteria survived and grew in numbers during the treatment, indicating that the prepared metal–carbon composite was non-toxic and conducive for the bacterial growth. The treated oils separated from the solid adsorbents, were found to be free from bacteria. Furthermore, both adsorptive and bacterial desulfurization were performed over the prepared Ni containing ACBs without necessity of removing the adsorbents from the liquid to be treated in the bacterial desulfurization step.

After the sequential adsorptive and bacterial desulfurization, the spent adsorbents were regenerated using *Enterococcus faecium* strain R5 and reused successfully up to three cycles of the hybrid method, with approximately 97% removal of DBT and 95% removal of TH in the last cycle. Therefore, bacterial regeneration showed an efficient removal of the S-containing compounds from the spent adsorbent surface at room temperature (~30 $^{O}$C) without requiring any expensive chemicals.

The novelty of the present study includes integration of two different desulfurization techniques namely adsorptive desulfurization and bacterial desulfurization in sequence for complete (99%) desulfurization of liquid fuels. Additionally, the spent adsorbent was bacterially regenerated using *Enterococcus faecium* strain R5. The process was found efficient up to three regeneration cycles.