

## CHAPTER V CONCLUSIONS AND RECOMMENDATIONS

## 5.1 Conclusions

In this study, the adsorbents used for desulfurization were prepared by impregnation of activated carbon and alumina with Cu<sup>+</sup> and Ni<sup>2+</sup>. Direct impregnation by using CuCl in acetronitrile solution was found to be unsuitable due to the stability and low solubility of Cu<sup>+</sup>. Impregnation was therefore performed with an aqueous solution of CuCl<sub>2</sub> following by a reduction step of CuCl<sub>2</sub> into CuCl using H<sub>2</sub>. For Ni<sup>2+</sup>, an aqueous solution of NiCl<sub>2</sub> was used. A suitable feed flow rate and granulometry of the adsorbent was found to be 0.4 cm<sup>3</sup>/min and 100 to 400  $\mu$ m, while the optimum temperature was 60°C and 90°C for  $Ni^{2+}$  and  $Cu^{+}$  impregnated on the adsorbent, respectively. The adsorption capacities at the sulfur breakthrough followed the order non-impregnated macroporous alumina  $< Cu^+/macroporous$ alumina < non-impregnated mesoporous alumina < Cu<sup>+</sup>/mesoporous alumina <  $Ni^{2+}/macroporous$  alumina  $< Ni^{2+}/mesoporous$  alumina  $< Cu^{+}/AC < non-impregnated$ AC. Ni<sup>2+</sup>/ and Cu<sup>+</sup>/ mesoporous alumina showed a higher breakthrough capacity of dibenzothiophene than 4,6-dimethyldibenzothiophene. A comparison of the breakthrough capacities of 4,6-dimethyldibenzothiophene, between Ni<sup>2+</sup> and Cu<sup>+</sup> impregnated on mesoporous alumina, showed higher adsorption capacity with Ni<sup>2+</sup> impregnated on mesoporous alumina than with Cu<sup>+</sup> impregnated alumina. In presence of polyaromatic compounds, the breakthrough capacities of dibenzothiophene were less than the system without polyaromatic compounds for both Ni<sup>2+</sup> and Cu<sup>+</sup> impregnated on mesoporous alumina, due to a competition between dibenzothiophene and polyaromatic compounds. The selectivity followed the order dibenzothiophene  $\approx$  phenanthrene > naphthalene. In presence of nitrogen compounds, the breakthrough capacities of dibenzothiophene were less than for the system without nitrogen compounds for both Ni<sup>2+</sup> and Cu<sup>+</sup> impregnated on mesoporous alumina, due to the stronger interaction between the metal and nitrogen atom. The selectivities followed the order acridine > carbazole > dibenzothiophene.

## 5.2 Recommendations

These results show an interesting effect of the  $Cu^+$  and  $Ni^{2+}$  toward the adsorption of dibenzothiophene and 4,6-dimethyldibenzothiophene. In order to try to improve the capacity and the kinetics of adsorption, several other parameters have to be studied.

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A variation of amounts of metal loading on the adsorbents should be studied to observe this effect on the sulfur adsorption capacities. Different types of impregnation such as dry and wet impregnation should be studied. Since the activated carbon cannot be wettable by water, ethanol is used instead of water. But  $CuCl_2$  can a little bit dissolve in ethanol. Thus the activated carbon is impregnated for several times. From this reason, it is not good for an economical point of view. Thus the other adsorbents preparations should be investigated.

Characterization of the adsorbents with other techniques, to study with more detail the metal dispersion, should be performed. Thermal desorption of probe molecule by thermogravimetry (TPR equipments) could be performed, with a comparison with the non-impregnated solids. X-ray diffraction techniques could also be used to characterize the deposit on the surface of the solids.

Due to the strong interactions between the metal on the adsorbents and sulfur or nitrogen atom in sulfur or nitrogen compounds, the kinetics of the adsorption is low. The adsorption temperature is a key parameter that can modify the kinetics of adsorption. Thus a variation of adsorption temperature should be studied.