Abstract

The present research focuses on nonconventional desulfurization techniques such as oxidative, extractive and adsorptive desulfurization of model fuel containing thiophenic sulfur compounds (thiophene, benzothiophene, dibenzothiophene). The activities of nano-hydroxyapatite, nano-Ag/TiO_2 and commercial TS- 1 as catalysts were explored in oxidative desulfurization. The performance of aqueous HCl, HNO_3, H_2SO_4, CH_3COOH, NH_4OH, NaOH, NaCl, were studied as solvents in extractive desulfurization. Coal dust, bentonite, fly ash, laterite soil and sodium zeolite were employed as adsorbent for adsorptive desulfurization. The surface morphologies of catalysts and adsorbents were characterized by different analytical techniques such as, TEM, XRD, FTIR, SEM, BET, DLS, XPS, XRF, EDS, UV-vis spectroscopy, TPR and TPD.

Nano hydroxyapatite (Hap) of 30-50 nm particle size was synthesized by green route using carrot peal extract. The highest conversion of 65% of thiophene in oxidation reaction was observed in glass batch setup with nano-Hap catalyst, but impregnation of titanium and molybdenum in nano Hap improved the conversion of thiophene significantly upto 82%. Langmuir-Hinshelwood (LH) model was proposed to explain the kinetics of the reaction.

In another work, silver nano particle with size ranges 20 to 50 nm was prepared from silver nitrate using tulsi leaf extract and impregnated in TiO_2 for oxidation of thiophene in batch setup. Both pseudo-homogeneous and heterogeneous kinetic models were proposed, and Langmuir- Hinshelwood kinetic model is established with irreversible surface reaction as rate controlling step.

The influence of different hydrocarbon components (isooctane, benzene, cyclohexane and n-octane) in the model fuels on the oxidation of thiophene using commercial TS-1 as catalyst was observed in batch system. The deactivation of catalyst in this process was studied and the deactivation mechanism was assumed to be independent in nature, with proper fitting of the experimental data.

Extraction of thiophene (TH), benzothiophene (BT) and dibenzothiophene (DBT) from iso-octane phase was studied using aqueous acidic, alkaline and salt solutions of different

concentrations. Aqueous hydrochloric acid showed best performance as solvent for extraction, whose maximum sulfur removal efficiency towards thiophene, benzothiophene and dibenzothiophne were found to be 50, 28.2 and 26.8% respectively. LLE[liquid-liquid equilibria] data of ternary mixture{thiophene+isooctane+HCl water solution} were collected at 40, 50, 60 and 70 ^{o}C at atmospheric pressure and correlated with Othmer-Tobias and Hand Correlation.

The performance of coal dust as an adsorbent for desulfurization of model fuel (model sulfur compounds: thiophenol, benzothiophene, dibenzothiophene and model aromatic compounds: benzene, toluene) in batch process was investigated and that performed quite good among many other naturally obtained adsorbents (bentonite, fly ash, laterite soil and sodium zeolite). The process parameter optimization was done by response surface methodology using Box-Behnken design (BBD).

Keywords:- Oxidation, nano-hydroxyapatite (Hap), nano-Ag/TiO_2, green synthesis, kinetics, deactivation, TS-1, extractive desulfurization, adsorptive desulfurization, Box-Behnken design (BBD)