ADSORPTION OF SULFONE COMPOUNDS IN THE OXIDATIVE DESULFURIZATION PROCESS USING ACTIVATED CLAY: EQUILIBRIUM AND KINETIC STUDY

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The inevitable and incessant combustion of diesel fuel has been proven to continuously produce more particulates and other harmful pollutants. Studies showed that combustion of diesel fuel produces precursors of sulfuric acid which causes ecosystem destruction such as acidification of bodies of water and destruction of crops and sulphate which is the main component of harmful respirable particles in the atmosphere (Alhamed and Bamufleh, 2008; Collins, 1997; Duarte *et al*., 2011). In order to alleviate these negative impacts, environmental laws on sulfur content of diesel fuel were enacted all over the world. In most developed countries like United States, Japan and Europe, the maximum sulfur concentration in highway diesel was limited to 15 ppm(Anisimov and Tarakanova, 2009; Babich and Moulijn, 2002; Bakar *et al*., 2012; Stanislaus *et al*., 2010; Sundararaman and Song 2010).

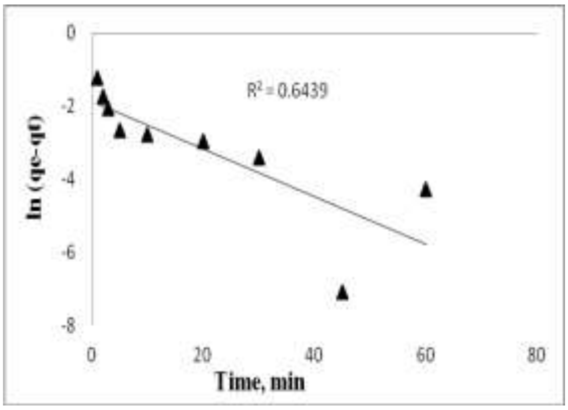
In diesel, the primary sulfur compounds that need to be removed in reducing its sulfur content are comprised of benzothiophene (BT), dibenzothiophene (DBT), and their alkyl derivatives (Anisimov and Tarakanova, 2009). Over the convention hydrodesulfuzation (HDS), oxidative desulfurization (ODS) was studied to be more cost-effective and more efficient in oxidizing the refractory compounds, predominantly, 4, 6-disubstituted dibenzothiophenes (DBT) (Alhamed and Bamufleh, 2008; Chica *et al*., 2006; Feng, 2009; Gatan *et al*., 2004; Liotta and Han, 2003; Wang *et al*., 2003; Zhang *et al*., 2009; Zhou *et al*., 2009). Generally, there are two main reactions involved in ODS process. First, the divalent sulphur atom of the organic sulphur compounds undergoes electrophilic addition of oxygen atoms from the catalyst to form the sulfone (Chica *et al*., 2006). Then, the formed sulfone having different chemical and physical properties from those of fuel oil hydrocarbons is removed through conventional separation techniques such as distillation, solvent extraction, adsorption, and decomposition (Alhamed and Bamufleh, 2008). This study is focused on the removal of sulfone from oxidized diesel using activated clay through adsorption.

In this study, oxidation of diesel was done using a high-shear mixer (IKA Ultra Turrax T25 digital) set at 15000 rpm for 30 minutes. Diesel fuel (1109.3 ppm S) was mixed with tetraoctylammonium bromide, TOAB (98%, Merck) and hydrogen peroxide, H2O2 (50 %, Merck) containing phosphotungstic acid, HPW (98%, Merck). After mixing, the oil phase which is the oxidized diesel was decanted from the mixture. To further remove the sulfur containing compounds found in the oxidized diesel, it was processed in a batch adsorption method. Activated clay was used as an adsorbent. The sulfur content of diesel in every stage of the oxidative desulfurization process was analyzed using total sulfur analyzer, SLFA 2100 Horiba. The data resulting from this experiment was used for the evaluation of adsorption isotherm and kinetic study.

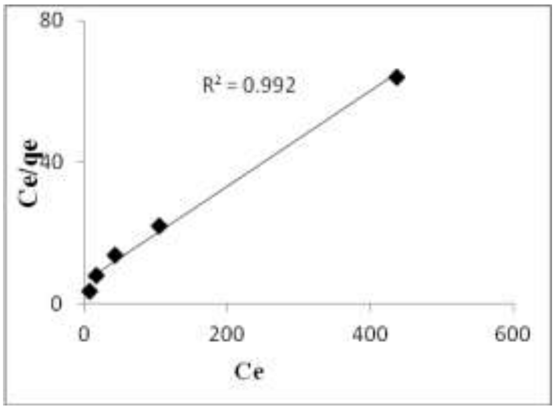
The controlling mechanism of the adsorption process was verified through the different adsorption kinetics models (Chen *et al*., 2012).. In this study, experimental data were fitted to pseudo-first and pseudo-second order rate reaction as shown in figure 1.

The correlation coefficients R^2 from resulting graphs were compared to verify the acceptability of the models. Based on figure 1, pseudo-second order model has a high R2 value (0.997) compared with pseudo-first order R2 value (0.6439). This indicates that adsorption of sulfone onto activated clay is well explained by pseudo-second order rate model. As pseudo-second order rate model fitted well the adsorption of sulfone compounds onto activated clay, it means chemisorption is the rate-limiting step. Therefore, the adsorption process is dominated by physical adsorption. Physical adsorption describes that the intermolecular attraction between sulfone compounds and activated clay particles is governed by van der Waals force.

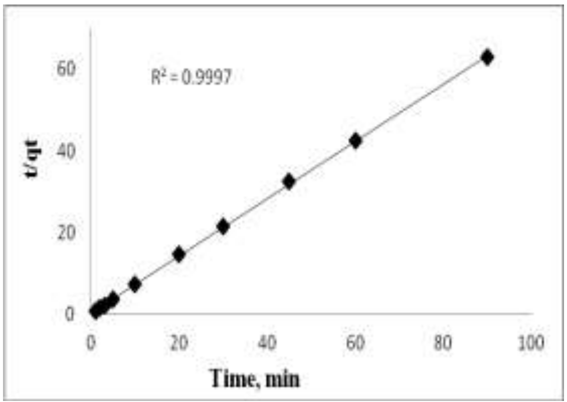
In addition, comparing the correlation coefficient of the two isotherms, Langmuir better represents the adsorption of sulfone better. Isotherms describe the interactive behaviour of adsorbate and adsorbent. Therefore, the adsorbate forms a monolayer on the surface of the adsorbent.



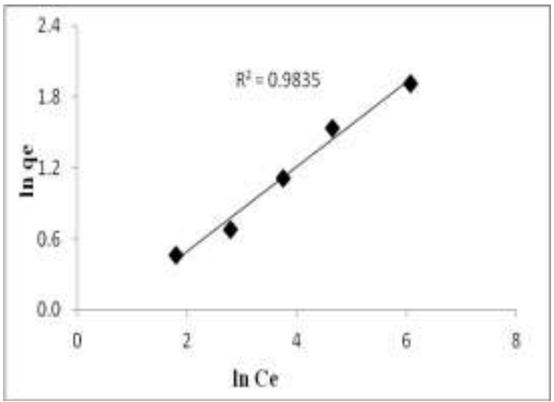
(a)



(a)



(b)



(b)

Figure 1: Adsorption Kinetic Study fitted on (a)pseudo-first order and b) pseudo second-order

Figure 2: Adsorption Isotherm study based on (a) Langmuir and (b) Freundlich

Keywords: Oxidative Desulfurization, Sulfone, Adsorption, Activated Clay, Diesel

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