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ADSORPTION OF PHENOL BY OIL SHALE AND FCC SPENT CATALYST: KINETIC, EQUILIBRIUM AND THERMODYNAMIC STUDIES

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Oil shale and petroleum industries are well-known to produce a large amount of residues. The Brazilian oil shale industry can generate up to 7,000 ton per day of by-products, such as pyrolyzed oil shale and oil shale fines, which are turned back to the mine with no utilization. The world production of spent fluid catalytic cracking (FCC) is around 400,000 ton per year. Most of them are usually solidified and deposit in landfills [1].

Hence, the present work was aimed at study the adsorption of phenol by oil shale and spent FCC catalyst residues. The oil shale samples used in this study were obtained from PETROBRAS units: (FOS) Oil Shale Fines; (POS) Pyrolyzed Oil shale; (TOS) pyrolyzed Oil Shale with Tire dosage (about 5%); spent FCC (CAT). All samples were dried for 24 hours without any activation. The adsorption experiments were carried out as a function of different initial phenol concentrations under the room temperature ($\approx 25^\circ\text{C}$), 20°C and 60°C . The kinetic study was conducted using a jar test apparatus at room temperature of 15 min to 24 hr based on the equilibrium time previously obtained. The Freundlich and Langmuir models were adjusted to equilibrium data through non-linear regression using trust-region and robust bisquare algorithms. The description of the adsorption process was given by a Homogeneous Surface Diffusion Model (HSDM). The original HSDM was developed for the granular active carbon adsorption process simulation. Later it was adapted to use with powdered activated carbon [2,3]. The HSDM estimated the Diffusion coefficient (D_s) according to the analytical solution proposed by Crank [4] and Skelland [5] and using the numerical optimization technique [6].

In general, the equilibrium data fitted well to both Freundlich and Langmuir adsorption models. The thermodynamic results indicated that the increase of the temperature did not favored the adsorption process to FOS ($q_m = 1.30$ to 0.91 mg g^{-1}) and favored to POS ($q_m = 2.60$ to 3.37 mg g^{-1}), TOS ($q_m = 1.28$ to 3.44 mg g^{-1}) and CAT ($q_m = 0.78$ to 1.41 mg g^{-1}), which were confirmed by the Gibbs energy and CAT ($q_m = 0.78$ to 1.41 mg g^{-1}), which were confirmed by the Gibbs energy. The positive values of enthalpies to POS, TOS and CAT were obtained which indicated the endothermic nature of the adsorption process. The enthalpy value was more significant in TOS (142.32 kJ mol^{-1}) and CAT (84.07 kJ mol^{-1}). Nevertheless FOS presented a negative value of enthalpy (-43.91 kJ mol^{-1}). This confirmed the

endothermic nature of the adsorption process ($\Delta H < 0$). A positive value for ΔS and ΔG of endothermic processes [7]. In this study, ΔS assumed positive values for (POS, TOS and CAT were related to an increase in the degree of freedom of the adsorbed species [8]. A positive value of ΔS suggested increased randomness at the ΔS /solution interface with more effective action among adsorbate and adsorbent surface active sites. The diffusion coefficient (D_s) confirmed factorially the experimental data. FOS sample presented higher value than others reagents from oil shale residues (FOS = $9.9E-8$ cm² min^{-1}) and CAT showed the $1.0E-8$ cm² min^{-1} . The presented study showed that the oils shale and spent catalyst FCC have a relatively good removal of phenol from aqueous solution and may be used for environmental purposes.

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