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Lignosulfonates Adsorption onto Clay as Sacrificial Agent –  
Benchmarking for Enhanced Oil Recovery

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## Research Highlights

This study is to investigate the adsorption capability onto kaolinite for different types of lignosulfonates in various salinity environment. Depletion method using the UV-Vis were used for measuring the concentration of lignosulfonate before and after the adsorption process in equilibrium and kinetic conditions. The highest amount of lignosulfonate adsorbed portrayed the best sacrificial agent that can be used in enhanced oil recovery application. The highest amount adsorbed of lignosulfonate onto kaolinite can prevent the surfactant lost into the formation. Among the four tested lignosulfonates, sodium lignosulfonate appeared the best in terms of adsorption capability in the presence of NaCl and CaCl<sub>2</sub> salt in the system. Freundlich isotherm model was the best to describe the equilibrium adsorption data of sodium lignosulfonate. On the other hand, pseudo-second order model was the best to describe the kinetic adsorption data of sodium lignosulfonate.

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## Research Objectives

The objectives of the research are to investigate and compare adsorption capability of four different type of lignosulfonate; sodium lignosulfonate, ammonium lignosulfonate, magnesium lignosulfonate and calcium lignosulfonate onto kaolinite. The adsorption capability was furthered investigated in equilibrium and kinetic conditions with the presence of various salinity and pH. Significant of this research is to fill the gap of why and which type of lignosulfonates were chosen as sacrificial agent to reduce the surfactant adsorption during the application of enhanced oil recovery. To the best of the author knowledge, no literature review reported the comparison of various lignosulfonates on the adsorption capability. As such, this research can be applied as a benchmark to select the most effective sacrificial agent towards reducing surfactant adsorption, particularly onto kaolinite.

## Methodology

Adsorption experiment had been conducted in two conditions: equilibrium and kinetic. For equilibrium test, 10g of kaolinite with 50ml of lignosulfonate solution were put into 100ml bottle and was shaken for 24 hours and left undisturbed for 48 hours. As for the kinetic, the





mixture was shaken and sample collected at the designated time interval until concentration of lignosulfonate achieved constant. Depletion method (Wu et al., 2017) using UV-Vis to measure the lignosulfonates concentration before and after adsorption. The difference between the initial and after adsorption gave the amount of lignosulfonate adsorbed in mg/g. Lignosulfonate solutions with different concentrations were prepared and calibration curves were obtained. By using the established calibration curve, each lignosulfonate concentration can be calculated. Parameters tested in the adsorption experiment included the lignosulfonate concentrations (100ppm, 200ppm, 300ppm, 400ppm), salinities (1wt% of NaCl and 0.1wt% of CaCl<sub>2</sub>) and pH variations (3,5,7,9,11). The best selected lignosulfonate were further investigated in deionised water, 3wt% of NaCl and 0.5wt% of CaCl<sub>2</sub> in equilibrium and kinetic condition. Langmuir, Freundlich and Temkin isotherm models (Ahmadi & Shadizadeh, 2015; Bera, Kumar, Ojha, & Mandal, 2013) were employed to investigate the equilibrium adsorption data. Pseudo-first order, pseudo-second order and intra-particle diffusion model were employed to investigate the kinetic adsorption data.

## Results

In 1wt% of NaCl, sequence of sodium lignosulfonate>ammonium lignosulfonate>calcium lignosulfonate>magnesium lignosulfonate had been obtained. In 0.1wt% of CaCl<sub>2</sub>, sequence of sodium lignosulfonate>ammonium lignosulfonate>magnesium lignosulfonate>calcium lignosulfonate was observed and in the both systems, sodium lignosulfonate appeared the most appealing lignosulfonate in terms of adsorption capability. In the system of monovalent 1wt% NaCl, the kaolinite surface remains negatively charge (Bai, Wu, & Grigg, 2009) and anionic lignosulfonate caused the repulsion electrostatic. Sodium lignosulfonate and ammonium lignosulfonate both having same ion counter had weaker repulsion electrostatic compared to ion counter in calcium lignosulfonate and magnesium lignosulfonate, thus increased the adsorption. When the system become divalent with 0.1wt% CaCl<sub>2</sub>, the zeta potential of the kaolinite surface increased positively (Bai et al., 2009; Jian et al., 2018; Parsons & Ninham, 2010). The sodium lignosulfonate and ammonium lignosulfonate had stronger attraction electrostatic compared to calcium lignosulfonate and magnesium lignosulfonate, so the adsorption increased. Among sodium lignosulfonate and ammonium lignosulfonate, sodium lignosulfonate appeared the most favourable onto kaolinite. The sequence of adsorption capacity under the influence of varying pH in 1wt% NaCl were obtained as follows: sodium lignosulfonate>ammonium lignosulfonate>calcium lignosulfonate>magnesium lignosulfonate. The effect of salinity was observed to be more dominant than the pH effect on the lignosulfonate adsorption onto kaolinite. The selected sodium lignosulfonate was furthered investigated and result show that adsorption of sodium lignosulfonate onto kaolinite increased with the increased of the salinity. Freundlich isotherm and pseudo-second order best represented equilibrium adsorption data and kinetic adsorption data respectively.





## Findings

The sequence of the lignosulfonates adsorption capability onto kaolinite in the presence of NaCl, CaCl<sub>2</sub> and various pH are sodium lignosulfonate > ammonium lignosulfonate > calcium lignosulfonate or magnesium lignosulfonate. Sodium lignosulfonate appeared the best in adsorption ability. Effect of salinity in terms of adsorption capability seem more prominence compared to pH. When salinity concentration increased, adsorption of sodium lignosulfonate were increased. Freundlich isotherm and pseudo-second order best represented equilibrium adsorption data and kinetic adsorption data respectively. Sodium lignosulfonate was recommended as a best sacrificial agent due to its ability to adsorb into the formation thus reducing surfactant adsorption during the application of enhanced oil recovery.

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