DESORPTION OF ETHYL ACETATE FROM MODIFIED CLAYS BY SUPERCRITICAL CARBON DIOXIDE

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Abstract **- The supercritical regeneration with carbon dioxide of modified and unmodified clays was experimentally studied after their use to adsorb ethyl acetate from aqueous solutions. Two quaternary amine modifiers (tetramethyl ammonium chlorine / TMA^+ and hexadecyltrimethylammonium bromide/ $HDTMA^+$) were used. The desorption of ethyl acetate adsorbed over the clays was performed with carbon dioxide at temperatures ranging from 301 K to 333 K and pressures ranging from 69.0 bar to 413.8 bar. The regeneration capacity was almost coincidental and high pressure was more favourable to regeneration. The effect of pressure and temperature was characterised under different conditions (gas, liquid and supercritical) and the supercritical has shown to be the best. A crossover effect was observed. The experimental data was fitted to a simple model, being the best results corresponding to desorption with carbon dioxide in its supercritical region.**

Keywords **- Organo-clay, smectite, adsorption, extraction, supercritical, carbon dioxide.**

I. INTRODUCTION

The unreasonable discharge of various chemical materials such as organic pollutants as industrial waste has been a major environmental concern. Therefore, the use of various physicochemical and biological techniques to remove these contaminants from wastewater has been extensively researched.

Supercritical fluid extraction has become widely accepted as a replacement for classical extraction methods mainly for environmental control. Chemical engineers are also tackling issues surrounding supercritical carbon dioxide, a promising, environmentally friendly replacement for organic solvents.

For the same reasons, research regarding new adsorbents for removal of pollutants from water has also been extensively done. The study of the regeneration of these adsorbents is also very important. The regeneration of activated carbon by supercritical carbon dioxide after adsorption of ethyl acetate had already been studied experimentally (Tan and Liou, 1988). Normally, the activated carbon is used to reduce and/or to recover organic compounds in effluent streams and ethyl acetate is one of these compounds commonly emitted by the chemical industry. Clay minerals as adsorbents, especially smectite, are of particular interest because of their large specific surface areas (Park and Yeo, 1999). An alternative adsorbent is modified clay. If a clay has metal cations occupying cation-exchange sites, its surface is hydrophilic because of the water molecules in the hydration shell solvating the cations. Such a surface is not a good adsorbent for removing hydrophobic organic molecules, which have poor water solubility (Boyd *et al.*, 1988). When the metal ions are replaced by large organic cations as those from surfactants, the nature of the clay surface is drastically altered, and turned hydrophobic or organophilic in nature. In other words, as hydrophobicity of the molecule is increased, the sorption of organics increases. The use of organo-clays as adsorbents for organic contaminants (both ionic and nonionic) from aqueous solutions has been studied. But works about desorption and regeneration using supercritical fluid conditions are scarce. In this work the regeneration of organo-clays loaded with ethyl acetate using supercritical carbon dioxide at different pressures and temperatures was studied. The clay employed was montmorillonite, and $HDTM^+$ and TMA^+ as organic modifiers were used, which gave different hydrophobic nature to the clay.

II. EXPERIMENTAL

Details about the experimental methods can be found in (Coelho *et al.*, 2001). The adsorption of $HDTMA^+$ and TMA^+ onto montmorillonite was performed in an amount just equal to the cation-exchange capacity of the clay. In order to examine the structural difference of montmorillonite before and after the modification with a quaternary amine, the basal spacings (d_{001}) were determined using a Powder X-ray diffractometer. In order to verify the adsorptive capacities of organically modified clays and to compare them with an unmodified clay, a batch experiment was designed.

In the adsorption experiments, the ethyl acetate solution (2.6 g/L) was pumped through the column packed with organo-clay (Fig.1). The ethyl acetate solution, at a temperature of 308 K, was passed through the packed bed and the concentration of the effluent was determined using solid phase micro-extraction – gas chromatography (SPME-GC). The column (2.7 cm^3)