Thesis of PhD dissertation

RETENTION OF PETROLEUM HYDROCARBONS ON DIFFERENT SORBENTS AND THEIR PHOTOOXIDATION IN SUSPENSION CONTAINING TiO_2 PHOTOCATALYST

Tímea Pernyeszi

PhD programme leader:
Dr. Imre Dékány
professor
corresponding member of the Hungarian Academic Science

Department of Colloid Chemistry, University of Szeged
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1. Introduction and objectives

The study of adsorption–desorption properties of asphaltenes as crude oil components on sorbents having different structure (lamellar clays, porous silicagel, reservoir rock samples) is significant. Partly because of the amount of adsorbed asphaltenes on soil components, reservoir rocks and displacement of asphaltenes plays an important role in IOR/EOR technology, and partly because of the analysis of asphaltenes/solid interactions, removal and degradation of crude oil hydrocarbons may also provide further progress in environmental chemistry.

Since it is difficult to remove and degrade asphaltenes from solid surface and these hydrocarbons also cause serious problems in oil production, transportation and refinery, first their adsorption properties and hydrophobizing effect were studied on soil components, different adsorbents with well-defined structure and natural formation rocks. Due to a pressure drop at the bottom hole of oil-wells, the asphaltenes and the paraffins deposit in the pores, decreasing thus the flow rate and, hence the oil production. Regarding to this phenomena and modelling subsurface conditions – where the temperature and the pressure are high – the removal (desorption) of crude oil components interacting with formation rock constituents was analyzed on porous sorbents. The different hydrocarbons from crude oils may get to the surface waters through transportation of crudes. Spill from oil pipes, tubes, reservoirs and tanks represents the serious problems, but in worse case they may also flood and contaminate wast amount of soil and ground water. Consequently, it is important to remove and degrade the crude oil components in aqueous medium of soil. For the implementation of these objectives the heterogen photocatalysis being as one of the most effective method was used which represents a rapidly developing research area, today.

The asphaltenes and heavy crude oil cuts adsorb strongly on different soil and rock types having various surface characteristics. To remove hydrocarbons from contaminated environment is particularly important in the following two areas:

- in oil production: the displacement of hydrocarbons from the surface of formation rocks,
- environmental protection: the decontamination of soils and groundwaters from hydrocarbons.

Referring to both fields mentioned above the objectives of the dissertation are the followings:

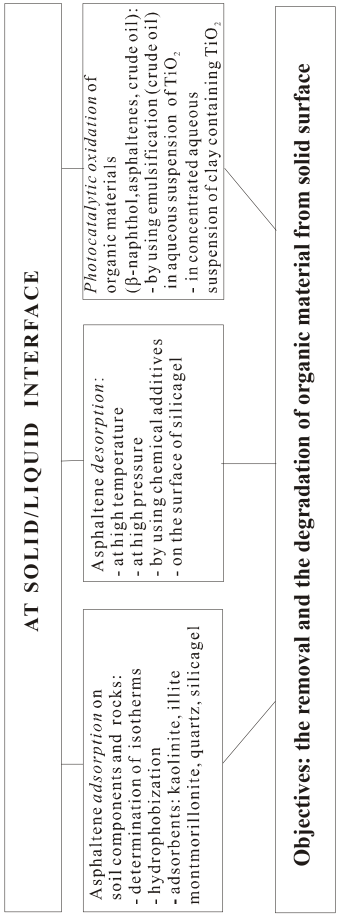
1. The analysis of structure, porosity and surface properties of various soil components (lamellar clays) and reservoir rocks by N_2-adsorption and small-angle X-ray scattering.

2. The determination of asphaltene adsorption isotherms from good (aromatic) solvent (toluene) and precipitating agent/solvent (n-heptane/toluene) mixtures at various concentrations.

3. The characterization of adhesion interactions, surface hydrophobization by adsorption and the changes in structure due to adsorption of asphaltenes by various structure-analyzing methods like N_2-adsorption, X-ray diffraction (XRD), small angle X-ray scattering (SAXS), microcalorimetry and infrared spectroscopy (FT-IR).

4. Analysis of the role of pressure (P = 10, 40 and 80 bar) and of additives as a peptizator in asphaltene desorption from porous surface under dynamic (flow) conditions at high temperature, T = 50, 90 and 150 ^oC.

5. Application of different emulsification techniques in photocatalytic oxidation of poorly soluble hydrocarbons in water. The study of removal and degradation of model-compound (β-naphthol) and environmental relevant compounds (asphaltenes and crude oil) at solid/liquid interface in concentrated aqueous suspension containing TiO_2/clay catalyst-mixture by determination of total organic carbon (TOC) content.



Objectives of dissertation

2. Experimental conditions

2.1. Materials

The asphaltene samples were prepared from crude oil derived from a well at the Algyő oilfield (Alg. 556 Ap 13/B, Southern Hungary) by n-hexane precipitation. Prior to adsorption experiments, the toluene and the n-heptane to be used as solvents were dried on a 0.4 nm molecular sieve (Merck AG).

The adsorbents for study of *asphaltene adsorption* were dried at 110 °C: The quartz, illite, kaolinite, montmorillonite and reservoir rocks derived from a depth of 1500–1600 m (A92 and SZRB, Southern Hungary). The Kieselgel 60 silicagel was dried at 140 °C (Merck AG, Germany) and the Kieselgel 60 was treated with methanol.

For *elution experiments at high temperature and pressure* the surface of Kieselgel 60 was modified by different amounts of asphaltene. Prior to adsorption and elution experiments, the toluene used as solvent was dried on a 0.4 nm molecular sieve (Merck AG.), 2.5, 5.0 and 10 v/v % N-methyl-pyrrolidone (Halliburton Co., Targon II., additive as asphaltene peptizer) solutions were prepared with toluene.

The photocatalytic degradation of organic materials was studied in concentrated aqueous suspension of clay containing TiO_2:

- crude oil derived from a well at the Algyő oilfield (Alg. 556),
- asphaltene prepared from toluene solution of crude oil heavy fraction obtained from a well at the Algyő oilfield (Alg. 556 Ap 13/B, Southern Hungary) by n-hexane precipitation, and
- saturated at 20 ± 0.5 °C aqueous solution with β-naphthol (2-naphthol, $C_{10}H_7OH$, analytical pure, Fluka).

During their laboratory experiments the TiO_2 P25 (Degussa) and the Na/Ca-bentonite (Süd-Chemie, Germany) were used as photocatalysts.

The *degradation of emulsified crude oils* was studied in the presence of H_2O_2 in dilute aqueous suspension of TiO_2 photocatalyst. For these experiments F2-crude oil derived from a well at the Algyő oilfield was emulsified in ultrafiltrated water at 0.25 m/m% concentration. The emulsions were stabilized by 20 minutes ultrasonic treatment.

The photocatalytic oxidation of *β-naphthol, asphaltenes and crude oil* was carried out *in the aqueous suspension of TiO_2/Na-bentonite catalyst-mixtures.* The samples were homogenized and pulped to paste like consistence with water. The amount of liquid (water content) was 25 %.

2.2. Methods

2.2.1. *Determination of N_2 adsorption isotherms*

Measurements of N_2 adsorption were carried out in a Micromeritics Gemini Type 2735 automatic sorptiometer (Micromeritics, USA) at - 195 °C. This method enables to register the adsorption and desorption isotherms automatically, and the pore size distribution of the adsorbent could be calculated from the desorption isotherm. The specific surface area was calculated by the BET equation; while the pore size distribution (10 – 500 Å) was determined from the desorption branch of the isotherm using Kelvin's equation.

2.2.2. *X-ray diffraction*

The X-ray diffraction measurements of the samples were performed by a Philips PW 1820 diffractometer (CuK_α, $\lambda = 0.154$ nm) in powder and suspension state. The basal distances were calculated from the peak positions by the Bragg equation using the PC-APD 3.5 automatic powder diffraction program with an accuracy of ± 0.01 nm. The asphaltene intercalation was controlled by *in situ* adsorption equilibrium on asphaltene/clay mineral complexes in a sample holder coated by Mylar film at 298 K.

2.2.3. *Small angle X-ray scattering*

The small angle X-ray scattering was measured by CuK_αX radiation (λ = 0.154 nm) generated in a PW 1830 generator. The primary beam was directed through a Ni-filter into a compact Kratky camera (type KCEC/3), in which the width and thickness of the beam was 20 mm and 80 µm, respectively. The measurements were performed in air atmosphere for 4–6 hours. The intensity of the scattered radiation was measured by a proportional detector (slit width 100 µm) controlled by a PW 1710 microprocessor, and SDC (Scattering Data Controlling) software, in an angle range of $2\Theta = 0.05 - 7^{\circ}$. Absorption intensities (A_S, A_B) were determined by the so-called moving slit method. The I(h) scattering function measured in the Kratky camera had to be normalized and then the background scattering was taken into consideration in order to determine the structural parameters.

2.2.4. *Determination of asphaltene adsorption isotherms*

The 0.2 – 0.3 g of adsorbents were immersed in 10–10 ml of asphaltene containing solution having various concentrations. Toluene/n-heptane mixtures were used as solvents and the batch type tests were carried out in simple test-tubes. The suspensions were agitated for ca. 24 hours. The equilibrium concentration in the liquid phase was determined by measuring the absorbance at λ = 600 nm by UVICON 930 spectrophotometer.

2.2.5. *Microcalorimetrical measurements*

The enthalpy of immersion ($\Delta_w H$) characteristic of the solid-liquid interfacial interaction, was determined with an LKB-2107 sorption microcalorimeter. In the wetting studies the adsorbents were pretreated at 423 K and evacuated (at 10^{-3} torr) then contacted by immersion liquid in the batch cell.

2.2.6. *Infrared spectroscopy measurements*

Prior to analyzing the organic materials sorbed on the surface of sorbents standard KBr (150 mg) pellets containing 10 mg of samples were prepared. The infrared spectra were recorded by a Bio-Rad Digilab Division FTS-65A/869 FT-IR spectrometer. To study photocatalytic oxidation diffuse reflextion technique was applied. During preparation of samples 20 mg of the solid material was homogenized with 300 mg of KBr.

2.2.7. *Dynamic desorption method used for displacement of asphaltenes at high temperature and high pressure*

The elution liquid (carrier phase) (toluene, 2.5, 5.0 and 10 v/v % N-methyl-pyrrolidone/toluene solutions) was injected through in LC column filled with adsorbents containing asphaltenes with a HPLC pump at P = 10, 40 and 80 bar inlet pressure. The temperature of column was kept at constant temperature (T = 50, 90 and 150 ^{o}C) with an automatic heating regulation apparatus. The eluent liquid was passing through column into the helical cooling, which was connected to a pressure regulating apparatus. Then the high pressure liquid expanded through a pressure regulator and with an electromagnetic valve the samples could be consequtively taken from the elution liquid. The concentration of asphaltenes in this liquid was determined by spectrophotometry after calibration measurement.

2.2.8. *The application of photocatalytic oxidation for partial removal of organic materials*

Photocatalytic oxidation in the dilute aqueous suspension of TiO_2 (0.1 m/v %): The photocalalytic experiments were carried out in a photoreactor (V = 350 ml) equipped with high-pressure mercury lamp (150 W) and intensive cooling (25 ± 0.5 ^{o}C) during the 10 hours irradiation tests.

In concentrated aqueous suspension of bentonite/TiO_2 catalyst-mixture: The photooxidation of organic materials was carried out in ceramic platter with 8 cm of diameter under ambient condition at about 15 mm of thickness of a layer. The samples were placed at about 25 cm from intermediate-pressure mercury lamp in a solar box equipped with a magnetic stirrer (HANAU 150 W, λ = 240–580 nm). After irradiation of the samples the carbon content was determined by TOC 1200 (Euroglas) analyzer. The RSD of TOC measurements was ± 1 %.

3. New scientific results and conclusions

A/ A*dsorption and desorption of asphaltenes on sorbents having various surface characteristics:* Studing the asphaltene adsorption on different clays (montmorillonite, kaolinite and illite), quartz, reservoir rocks, porous sorbent (silicagel) and using toluene as solvent, the following conclusions could be drawn:

1. The highest asphaltene adsorption was observed on kaolinite, while the adsorbed amount decreased in the order of illite→montmorillonite. The large adsorption capacity of asphaltenes on kaolinite was explained by its high surface charge density. The adsorption capacity on montmorillonite was less than on kaolinite and its maximal adsorbed amount (per gram of sorbent) was nearly identical as found on quartz. Further it was concluded that the asphaltenes were bound only on external surface of the sorbent due to low charge density of montmorillonite, and asphaltene penetration into the interlamellar space could not be detected. According to the XRD measurements asphaltene intercalation was impossible in the interlamellar space of swollen montmorillonite, and hence, the asphaltenes were only bound on the external surface.
2. Changes of the adsorbent structure, particularly the porosity significantly affects the adsorption and desorption process. Compared to the values obtained for lamellar clays the maximal adsorbed amount increased on porous sorbents, while it decreased on hidrophobic surface.

3. The solubility of asphaltenes depends on the polarity of the solvent. Asphaltenes can be characterized by a looser, more peptized structure in toluene solution, while in n-heptane/toluene a more aggregated structure develops owing to the presence of the precipitating agent. In n-heptane/toluene mixtures a two-stage isotherms characteristic to molecular and micellar adsorption steps were recorded on kaolinite and montmorillonite, suggesting the adsorption of single asphaltene molecules in the first stage and micellar or aggregated forms in the second one. Parallel with increasing concentration of the precipitating agent (n-heptane) the adsorption equilibrium was shifted, which resulted in a decreasing solubility of asphaltenes and increasing of adsorbed amount.

4. The surface area of clays and rocks containing sorbed asphaltene layer was less than that of their original forms. The pores were clogged by the adsorbed asphaltenes, and as a result less pronounced N_2-adsorption–desorption hysteresis was observed demonstrating the aggregating effect of asphaltenes. These results were confirmed by Porod presentation calculated from small angle X-ray scattering, since the correlation length increased for the porous system. According to microcalorimetry measurements the heat of immersion $\Delta_w H$ on kaolinite and illite confirmed the hydrophobizing effect of asphaltenes. On the basis of FT-IR analysis, in the range of CH-stretchings, the hydrophobizing effect of asphaltenes on kaolinite was more pronounced than on montmorillonite. As the amount of adsorbed asphaltene was increased, the bands characteristic (CH-stretchings) of asphaltenes appeared at higher and higher intensities in the spectra of asphaltene/clay organocomplexes.

5. The desorption is a practical method to remove asphaltenes from surface. Since the elution by toluene was not successful (effective), new experiments were carried out in a flow system operating at high temperature (T = 50, 90 and 150 ^{o}C) and high pressure (P = 10, 40 and 80 bar). In the case of experiments performed on porous silicagel the desorption of asphaltenes from the surface of silicagel (a model for soil components) was highly dependent on pressure and concentration of the peptizer (N-metyl-pyrrolidone) being an additive facilitating the solubilization of asphaltenes. In addition I found that efficiency of desorption was higher in toluene solution containing N-methyl-pyrrolidone than in pure toluene. Elution efficiency (synergetic effect) of the additive components could be explained by the effect of asphaltene peptization. The efficiency of asphaltene desorption was decreased by increasing of pressure due to inhibition of peptization.

B/ The photocatalytic oxidation of organic materials bound to the surface of sorbents by TiO_2 photocatalyst: Studying the photooxidation of emulsified crude oil in dilute aqueous suspension of TiO_2, β-naphthol, asphaltenes and crude oil in concentrated aqueous suspension of TiO_2/bentonite the following theses could be stated:

6. In the presence of H_2O_2 1 M concentration significantly increased the rate of degradation (about 50 %) at equivalent concentration of TiO_2.

7. In concentrated aqueous suspension of TiO_2/Ca-bentonite catalyst-mixture (25 m/v %), and in the case of photocatalytic degradation of β-naphthol dissolved in water, the degraded carbon content increased parallel with increasing of TiO_2 concentration and maximum efficiency was attained at 75–80 % of TiO_2 concentration in the catalyst-mixture. The degraded carbon content measured on pure TiO_2 was nearly equal to the value determined in the case of 50–70 % of TiO_2 concentration in catalyst-mixture. It was also shown that the pure Ca-bentonite possesses also a photocatalytic activity, since low degree of photocatalytic degradation was observed in its concentrated suspensions during UV-irradiation. According to FT-IR analysis the characteristic bands of β-naphthol disappeared, viz. amorphous material containing carbon remained and oxidized products with unsaturated bounds and linear structure were produced (aldehyde, ketone, carboxylic acid) on the surface of catalyst-mixture after two days of UV-irradiation. The spectra of natural chemical pure TiO_2 was determined after seven days of UV-irradiation.

8. According to photooxidation in concentrated aqueous suspensions by UV- and solar irradiation photodegradation of asphaltenes and crude oil is also significant, when Na-bentonite contaminated by hydrocarbons was mixed with TiO_2 in a ratio of 1:1. It was stated that both the crude oil and the asphaltenes degrade in the suspension of Na-bentonite. Therefore, the photocatalytic effect of clay was significant especially in the beginning of the process. This fact explains that the TiO_2/bentonite catalyst was more effective than the pure TiO_2 for degradation of hydrocarbons. Thus, in the case of crude oil synergetic effect occured. There was not significant difference between artificial and natural solar irradiation, the degraded amount of carbon increased to the same extent parallel with the time period of irradiation. The degradation of asphaltenes was very slow in the aqueous suspensions of all three catalysts due to the fact that apolar asphaltenes are such huge molecular mass components of the crude oil, which adsorb very strongly on the clays.

9. The FT-IR measurements verify the partial mineralization of crude oil hydrocarbons and total mineralization of β-naphthol. Thus carbon-dioxide and water are produced. Synergetic effect of clay minerals (Na- and Ca bentonite) on photocatalytic degradation can be explained by the large specific surface area (350–700 m^2/g) of the environmentally friendly sorbents and their adsorption properties.

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