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Solid effect in solvent extraction treatment of pre-treated oily sludge

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ABSTRACT

Oil recovery from oily sludge generated from the petroleum industry has been investigated by solvent extraction using four organic solvents, cyclohexane, *n*-hexanol, *n*-butanol and kerosene. Special emphasis was placed on the effect of sludge (solid) concentration (C_S) on the oil recovery efficiency (R_O) and partition coefficient (K_D). The K_D was found to vary with C_S. This phenomenon can be described as the "solid concentration effect" or "solid effect" (C_S-effect). The C_S-effect can be explained using the surface component activity (SCA) model that we developed previously. In this model, the activity coefficient of solid surface sites (f_S) was proposed as a function of C_S rather than unity because of interactions among solid particles. Based on the SCA model, we provide a C_S-dependent function of partition coefficient (termed the SCA-partition coefficient function), in which the intrinsic (or thermodynamic) partition coefficient $\left(K_D^0\right)$ independent of C_S can be simulated from extraction experimental data and can be used to characterize the extraction equilibrium. It was confirmed that the SCA-partition coefficient function could describe the C_S-effect observed in our solvent extraction experiments accurately. In addition, the f_S of the sludge was independent of the solvent in our tests and decreased with increasing temperature.

1. Introduction

Significant amounts of oily sludge are generated by the petroleum industry during crude oil production, transportation, storage and refinery processes. The oily sludge is a complex mixture typically containing 30–50 wt% oil, 30–50 wt% water and 10–12 wt% solids [1,2]. Because of its high oil content, oily sludge is considered to be hazardous to the environment and to human health and, in recent years, much work has therefore focused on its treatment [1–23].

Oil recovery is the most desirable environmental option for handling oily sludge as it has a high oil concentration, and from an economic point of view, oily sludge containing over 10 wt% oil merits the treatment [1,2]. Several techniques have been used to recover the oil, including flotation [1,3–5], freeze/thawing [2,6–10], sonication [2,11–15], electrical treatment [16], microwave radiation [8,17] and solvent extraction [18–23]. Among these methods, solvent extraction is an effective treatment and has the advantage of lower energy requirements [23]. In solvent extraction, the sludge-to-solvent mass ratio, or sludge (solid) concentration, is one of the important factors affecting the oil recovery efficiency [2,22,23]. Usually, the distribution coefficient (K_D), defined as the ratio of oil concentration in the solvent phase to that in the solid (sludge) phase at equilibrium, is used to characterize the solvent extraction equilibrium [23]. Zubaidy and Abouelnasr [23] investigated the fuel recovery from waste oily sludge using solvent extraction and demonstrated that the K_D increased with increasing solid concentration (C_S). Such a phenomenon has been described as the "solid concentration effect" or "solid effect" (C_S-effect) [24–26] and has been observed in numerous laboratories on diverse liquid–solid systems during studies on adsorption–desorption equilibrium at solid–liquid interfaces [24–37].

Thermodynamically, the K_D for a given system under constant temperature, pressure and medium composition (e.g., pH, ionic strength) should be independent of both oil and solid (sludge) concentrations. The change in K_D with C_S indicates that the experimentally measured K_D is not a thermodynamic equilibrium parameter. Many models have been developed to explore the fundamental mechanism of the C_S-effect and to describe the C_S-dependence of K_D, including the solute complexation model [26], the particle interaction model [29], the metastable-equilibrium adsorption (MEA) theory [38], the flocculation model [39], the power function (Freundlich-like) model [40] and the four components adsorption (FCA) model [41]. More recently, we developed a surface component activity (SCA) model [42–44], where the activity coefficient of solid surface sites is assumed to be a function of C_S rather than

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unity, because of the solid particle–particle interactions that exist in the real solid–liquid systems. Three C_S-dependent adsorption isotherms were derived from the SCA model and all can describe the C_S-effect observed in adsorption experiments [42–44].

In this work, we investigated solvent extraction of oil from oily sludge and the C_S-effect was observed. Using the SCA model, we analyzed the effect of C_S on K_D and derived a C_S-dependent function of the distribution coefficient, termed the SCA-distribution coefficient function or SCA-K_D function for clarity. The SCA-K_D function was used to fit the solvent extraction data and the results indicate that it can describe the C_S-effect observed in our experiments accurately. Furthermore, the effect of solvent and temperature on the activity coefficient of solid surface sites was investigated.

Uncertainties in the distribution coefficient at various C_S will limit the applicability of solvent extraction; for example, in the final design of single- and multiple-stage separation units for an extraction process [23]. Thus, an extraction model is required to describe the C_S-effect.

2. Experiments

2.1. Materials

Cyclohexane, *n*-hexanol and *n*-butanol were of analytical grade and kerosene was of chemical grade, purchased from Damao Chemical Reagent Co., China. Petroleum ether (boiling point 30–60 °C) was of analytical grade, purchased from Sinopharm Chemical Reagent Co., China. All chemicals were used as received.

Raw oily sludge was collected from Sinopec Shengli Oil Field, China. The sludge was sticky and consisted of 44.8 wt% oil, 28.6 wt% water and 26.6 wt% solids, analyzed by a mass-loss method as follows. Oily sludge (~10.0 g) was heated to 105 °C for 16 h in an oven (GXZ-9140 MBE, Boxun Industry Co., Shanghai, China). The mass lost from the sludge in this process was the water content. The reduction in mass by calcining the remaining dry sludge in a muffle furnace (DRI – 4 Resistance Furnace Temperature Controller, Huang Hua Comprehensive Electrical Appliance Factory, Hebei, China) at 600 °C for 3 h without covering by lid indicated the oil content in the sludge.

The sludge was pre-treated to remove most of the oil and water. The raw oily sludge was mixed with an equivalent volume of ~95 °C hot water and stirred vigorously for 30 min. After 2 days, any crude oil floating on the surface of the mixture was removed and the residue mixture centrifuged using a TD5-2 tubular centrifuge (Beili Centrifuge Co., Beijing, China) at 3000 rpm to remove most of the water. The obtained precipitate was mixed with an equivalent amount of cyclohexane by mass, stirred vigorously for 5 min, centrifuged at 3000 rpm for 5 min and the resulting precipitate dried at 105 °C to constant mass. The resultant product was used in this study and will simply be referred to as sludge [23]. After collection, the sludge sample was stored at room temperature.

The oil content of the sludge sample (5.00 g) was determined by calcination in an electrical muffle furnace at 600 °C for 3 h. The oil content in the sludge was 8.57 wt% based on the sludge mass loss.

2.2. Solvent extraction tests

Four solvents, cyclohexane, *n*-hexanol, *n*-butanol and kerosene, were used in this study. Known masses of sludge were added to 20.0 mL of the solvent, in which the C_S varied from 0.05–0.8 g mL^{-1}. The mixtures were shaken in a THZ-82 thermostatic water bath shaker (Wuhan Grey Mo Lai Detection Equipment Co., Wuhan, China) at a specified temperature (25.0, 40.0 or 55.0 °C) for 60 min. Solvent extraction kinetic tests indicated that the extraction time (60 min) is sufficient for the system to achieve full equilibrium (see Fig. S1 in Supporting Information). The remaining sludge samples were collected by centrifuging at 3000 rpm for 5 min, washing with ethanol and drying at 105 °C for 16 h in an oven. Their residue oil contents were measured using the petroleum ether extraction method (see Section 2.3). The oil recovery efficiency (R_O) from the oily sludge and the oil concentration (C_O) in the solvent were calculated from:

$$R_O = (\Gamma_{IO} - \Gamma_O)/\Gamma_{IO} \tag{1}$$

$$C_O = (\Gamma_{IO} - \Gamma_O)m/V \tag{2}$$

where Γ_{IO} and Γ_O are the initial and residue oil contents in the sludge (g g^{-1}), respectively, m is the mass of sand (g) and V is the solvent volume (mL).

Tests were conducted in triplicate and the final values were an average of the measurements.

2.3. Determination of sludge oil content by petroleum ether extraction method

The residue oil contents of the remaining sludge samples after solvent extraction were measured by a petroleum ether extraction method.

The sludge (0.500 g) was dispersed in 20.0 mL petroleum ether. The mixture was shaken in a THZ-82 thermostat water bath vibrator at 25.0 ± 0.5 °C for 20 min and centrifuged using a TD5-2 tubular centrifuge at 3000 rpm for 5 min. The oil concentration in the resulting centrifugate was determined by monitoring the absorbance at $\lambda = 227$ nm which is absorption wavelength of oil in sludge using a TU-1810 UV–Vis absorption spectroscope (Beijing General Analysis Universal Instrument Co., China) and calculated by regression analysis according to the standard curve obtained from a series of standard petroleum ether solutions of the oil. Based on the oil concentration in the centrifugate and the sludge mass used, the residual oil content of the sludge was obtained.

The oil content of the sludge sample before solvent extraction was also measured by the petroleum ether extraction method to be 8.43 wt%, consistent with the result from the calcination method.

2.4. Specific surface area and average particle diameter of sludge sands

After petroleum ether extraction, the residue solids were considered to be sands and their composition was not analyzed further. The specific surface area of the sands was measured by N_2 adsorption–desorption (Quadrasorb SI-MP system, Quantachrome Instruments, USA) to be 11.38 m^2 g^{-1}. The average particle diameter of the sands was measured by particle size distribution analysis (BT-9300H, Dandong Better Instrument Co., China) to be 340 nm.

2.5. Fitting error analysis

The experimental data fit to model equations was carried out using the non-linear least-squares method (Origin solver). Three fitting optimization parameters, the chi-square (χ^2) function, coefficient of determination (R^2) and fitting optimization index (I), were used to test the best-fitting parameter values in a model of the experimental data.

The functions χ^2 [45], R^2 [46] and I [47] can be represented as:

$$\chi^2 = \sum \frac{(x_{md} - x_{ex})^2}{x_{md}} \tag{3}$$