

The Adsorption of SDS on Ferro-Precipitates

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Abstract—The main aim of the paper is to evaluate ferro-precipitates as immobilization agents for removing selected surfactants from aqueous solutions. Two ferro-precipitates based on iron oxides were used. Adsorbents were varied both in elementary composition and mineral composition. Sodium dodecyl sulphate (SDS) was used as a model anionic surfactant. Simultaneous measurements of the surfactant's adsorption and zeta potential determination of the (adsorption) suspensions were carried out. The adsorption isotherms were found to be of typical Langmuir type; values of the SDS adsorption capacities were calculated (0.21 mmol/g for SDS on sample 1 and 0.44 mmol/g for SDS on sample 2, respectively). The shape of the adsorption isotherms was correlated with zeta potential values at the adsorption equilibrium. The addition of SDS affects the value of ζ - potential, making the zeta potential values more negative.

Keywords—ferro-precipitate, adsorption, SDS, zeta potential

I. INTRODUCTION

SURFACTANTS are commonly used in many industrial and commercial products and processes over the world. For example, surfactants are in demand for industrial processes requiring colloid stability, metal treatment, mineral flotation, oil production, emulsion polymerization, pesticides, and pharmaceutical formulation. This is a positive role of surface active agents, but their applications can produce environmental pollution and increase a series of problems for wastewater treatment plants [1]. Recently, efforts have been made to eliminate the content of various surfactants by means of adsorption on various types of adsorption materials.

Many materials have been studied as surfactant adsorbents, e.g. carbon black, chitosan, latex, chrysotile, montmorillonite, kaolinite, shungite, titania, and bentonite [2]-[9]. The second category is waste materials, e.g. various kinds of sludge. Other interesting adsorbents also offering good prospects are ferro-compounds such as hematite [10]. These oxy-ferro-compounds also occur as waste products in particular manufacturing processes; e.g. in the company Bochemie (Czech Republic), zinc chloride is manufactured particularly from recycled acid, which represents waste from zinc works. The problem of this production is the thick and almost unsettling sediment of iron which, moreover, retains rather

large amounts of zinc chloride. The sludge consists of approximately one third water, one third zinc chloride and the rest is ferro-compounds. Due to the presence of zinc chloride, the sludge cannot be used to charge a blast furnace. The solution is to find a suitable process of precipitating iron in solutions, e.g. using the goethite process. The goethite process is successfully used in the electrolytic galvanization industry to turn the iron in a solution (mostly sulphide or chloride) into a sediment which is easy to filtrate [11], [12]. The Electrolytic Zinc Company of Australasia developed a continuous process, during which all ferrous ions in a solution are at first oxidized, and subsequently the solution continuously flows into a reactor at a speed which eliminates the solid phase [13].

This method was also used to precipitate iron from the waste acid used to produce zinc chloride by Bochemie. The process was carried out under varied conditions (temperature, pH) and resulted in sediments with varied composition and texture parameters. Sediments high in zinc, further use of which is rather limited, were analyzed with regard to their possible use as sorbents to eliminate surfactants from aqueous solutions.

Different adsorption mechanisms and models have been suggested, depending on the adsorbent-adsorbate system. Below the critical micelle concentration when ionic surfactants behave as a single amphiphilic ion there are generally two possible interactions between adsorbent surface and surfactant molecules. Surfactants can be caught on the adsorbent through hydrophobic interactions, by their hydrocarbon coil, or through electrical forces, by their ionic groups. The predominance of one kind of interaction between the adsorbent and the ionic surfactant in the adsorption process is determined by the surface characteristics of the adsorbent. Hydrophilic adsorption of surfactants was found in three Australian coals [14]. However, measuring the zeta potential of active coal and carbon blacks in the presence of surfactants led to the idea that the interactions are mainly of a hydrophobic character [15], [16].

The main goal of this study was to judge waste materials on the basis of ferrous oxides as adsorption material to eliminate selected surfactants from solutions. Further goals were to describe the adsorption process by means of some adsorption theory (Langmuir, Freundlich) and to calculate the adsorption capacity of the sorbents. By means of the zeta potential, changes on the surface of adsorption particles were monitored during the adsorption process and on the basis of experimental data (adsorption amount, zeta potential and characterization of precipitates); a mechanism of surfactant adsorption was proposed.

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II. EXPERIMENTAL METHODS

A. "Goethite" Process

A continuous flow reactor was used in this process. 800 g of zinc chloride solution was put into a reaction vessel (filtering flask). The solution had been prepared by dissolving 240 g of solid zinc chloride in 560 g of distilled water. Recycled acid was purged of solid impurities by filtering it through a textile filter. Subsequently, all ferrous ions were oxidized into ferric ions by slowly adding hydrogen peroxide (30%) and continuously stirring the substance. Occasional checks were carried out to find out whether all the iron had oxidized. The discharge of oxidized acid into the reaction vessel was set on a peristaltic pump. A pH electrode, a stirrer and hoses from both pumps (with oxidized recycled acid and a zinc oxide suspension) were immersed in the reaction vessel. The stirrer was switched on. After having reached the desired temperature of 80°C and pH = 2.2 (sample 1) or pH = 1.0 (sample 2), both pumps and a computer program for pH were switched on. This way, the experiment began. The experiment finished after three hours. It is necessary to mention that we tested various conditions (temperature, pH, time), but in this paper will only discuss adsorption on materials which have been prepared under the conditions described above.

B. Adsorbents

The content of iron and zinc in the sediment created by the abovementioned process was determined. Surface area (BET) was determined as well and the sample was analyzed by RTG diffraction. The results are summarized in table 1.

TABLE I
PROXIMATE ANALYSES, SURFACE AREA AND MINERAL COMPOSITION

Sample	Fe %	Zn %	S ^{BET} m ² /g	RTG diffraction
1	55.2	7.4	220.5	ferrhydrite + feroxyhite
2	55.4	0.8	30.0	akaganeite

The surface area of the sample from the adsorption isotherms of nitrogen (SBET) was evaluated according to BET theory, using a nitrogen molecular area of 0.162 nm² for the calculation.

The normal powder XRD patterns were recorded between 5.0° and 50.0° 2θ using CuKα1 radiation with an INEL CPS 120 diffractometer equipped with a curved position-sensitive detector, in transmission mode with a germanium monochromator.

C. Chemicals

The chemicals used in this study were zinc chloride, zinc oxide, hydrogen peroxide, sodium hydroxide, hydrochloric acid and SDS. All the solutions were made with distilled water. Analytical grade chemicals were used. Critical micelle concentration (CMC) of SDS was determined by conductivity measurements.

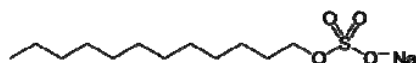


Fig. 1 Structure of SDS

D. Batch experiments

About 0.2 g of dried sample was added to 50 mL of a given surfactant solution of known concentration varying in the range 10-0.1 mmol/l and occasionally shaken. Adsorption equilibration took about 3 days, as deduced from previous measurements. The zeta potential of the adsorption suspensions was measured. Then, the sample was removed by filtering through filter paper. The surfactant concentrations of the filtered solutions were determined by UV-VIS spectrometry.

The amount of surfactant adsorbed (*a*) was calculated from the change in the solution concentration before and after equilibrium, according to:

$$a = \frac{(c_0 - c_e)V}{m} \quad (1)$$

where *c*₀ is the initial concentration of surfactant solution, *c*_e the concentration of surfactant solution at the adsorption equilibrium, *V* the volume of surfactant solution and *m* the mass of the sample.

E. Zeta Potential Measurements

Zeta potential was measured by analyzing 0.2 g of precipitate in 50 ml of surfactant solution using the Zetasizer Nano ZS (Malvern Instruments Ltd., GB). This machine uses Laser Doppler Velocimetry to determine the electrophoretic mobility. The zeta potential was obtained from the electrophoretic mobility by the Smoluchowski equation:

$$\zeta = \frac{\mu\eta}{\varepsilon} \quad (2)$$

ζ is the zeta potential (V), η represents dynamic viscosity (Pa.s), and ε stands for the dielectric constant. The fixed conditions of measuring were the following: temperature (298 K), electric field (15 V), frequency (500 Hz), and the properties of the samples – viscosity (0.0089 kg/m.s), refraction index (1.333), and dielectric constant (78.36).

III. RESULTS AND DISCUSSION

A. Characterization of Samples

Data from RTG diffraction show that sample 1 contains a significant amount of amorphous phase; the following two ferrous compounds are present – ferrhydrite Fe₅O₇(OH).4H₂O (30%) and feroxyhite δ-FeO(OH) (20%). The relatively high content of zinc makes disposal of this material (waste) in a blast furnace impossible. On the other hand sample 2 contains only 0.8% of zinc and the mineral composition is also different. This sample contains mainly akaganeite β-FeO(OH) (54.5). Sample 1 has approximately seven times higher specific surface area in comparison with sample 2 (see table 1). In addition we followed the influence

of pH on the zeta potential of our samples.

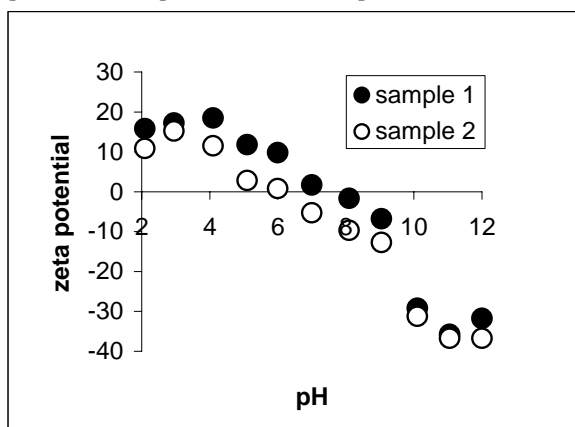


Fig. 2 Isoelectric points of samples, influence of pH on zeta potentials.

Figure 2 shows us differences in so-called isoelectric points when the value of zeta potential equals zero. Sample 1 reached zero at pH 7.5 contrary to sample 2 at pH 6. All adsorption experiments were carried out at pH 6 when the zeta potential of sample 1 was approximately +10 mV while the zeta potential of sample 2 was, as mentioned, zero.

B. Critical micelle concentration of SDS

Below the *CMC*, the addition of surfactant to an aqueous solution causes an increase in the number of charge carriers (Na^+ (aq) and $\text{OSO}_3\text{C}_{12}\text{H}_{25}$ (aq)) and consequently, an increase in the conductivity. Above the *CMC*, further addition of surfactant increases the micelle concentration while the monomer concentration remains approximately constant (at the *CMC* level). Since a micelle is much larger than an SDS monomer it diffuses more slowly through the solution and so is a less efficient charge carrier. A graph of conductivity against surfactant concentration is thus expected to show a break at the *CMC* (Fig 3).

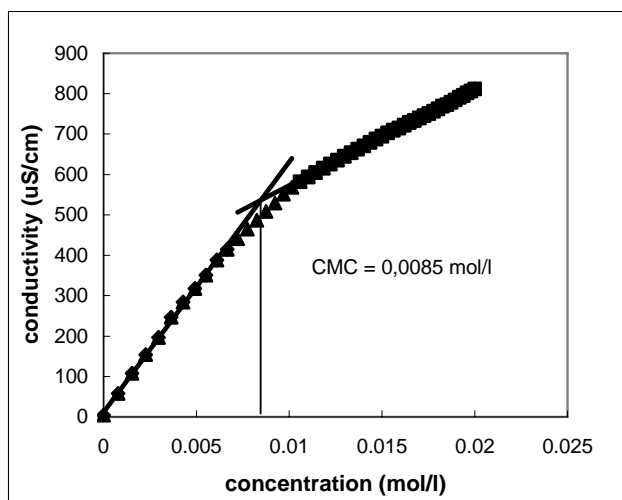


Fig. 3 Determination of SDS critical micelle concentration

As is obvious from figure 3, the value of *CMC* for sodium dodecyl sulphate is 8.5 mmol/l. There is no marked change in adsorbed amount of SDS at concentrations exceeding the level of the critical micelle concentration (figure 4).

C. Adsorption of Surfactant

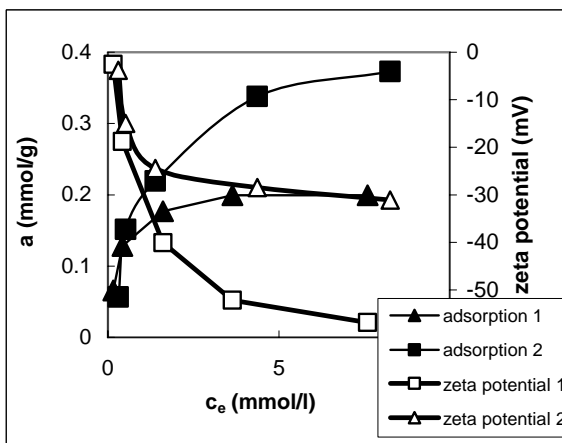


Fig. 4 Dependence of zeta potential (blank symbols) and adsorption of SDS (full symbols) on ferro-precipitates on the equilibrium concentration of the SDS solution (c_e).

Figure 4 depicts typical adsorption isotherms obtained from the experimental data. The shape of isotherms indicates that the adsorption data could be well fitted by the Langmuir adsorption model of monolayer coverage. In a linear form, the Langmuir equation is given by

$$\frac{c_e}{a} = \frac{c_e}{a_m} + \frac{1}{a_m b} \quad (3)$$

where a is the amount of the surfactant adsorbed, c_e is an equilibrium concentration of the surfactant in solution, b represents a monolayer binding constant and a_m is the monolayer adsorption capacity.

All adsorption isotherms proved to be consistent with the Langmuir model as deduced from calculated r -squared values close to 1 (minimal r^2 value was 0.987). The most informative parameter in the Langmuir equation is a_m , providing information on the adsorbed amount at monolayer surface coverage. These values are compiled in table 2 as found for studied samples. There are also comparable parameters of Freundlich adsorption isotherms:

$$a = k.c_e^{1/n} \quad (4)$$

where k and n are dimensionless Freundlich constants.

TABLE II
RESULTS OBTAINED FROM THE LANGMUIR AND FREUNDLICH EQUATIONS
APPLIED TO THE ADSORPTION DATA

Sample	Langmuir isotherm			Freundlich isotherm		
	a_m (mmol/g)	b (l/mmol)	r^2	k	n	r^2
1	0.207	3.706	0.999	0.135	3.650	0.860
2	0.443	0.674	0.987	0.152	1.968	0.860

From table 2 it is obvious that SDS adsorption on sample 2 is approximately two times higher in comparison with sample 1. These results are surprising because sample 1 has a markedly larger specific surface area (see table 1). It seems that the specific surface area does not play the most important role in the immobilization process and specific interactions between iron minerals and surfactant molecules probably exist. The reason for the higher adsorption capacity of sample 2 we can find in its different zeta potential value. At pH 6 (value for all studied systems), the surface of sample 2 is without charge and is easy accessible for the hydrophobic part of surfactant molecules. On the other hand, the charge on sample 1's surface can act as a barrier against SDS adsorption. So from the zeta potential measurements as well as from the surface characteristics of the precipitate, it was deduced that the sorption mechanism of SDS on the adsorbent surface is connected mainly with interactions between the hydrophobic part of the surfactant and the precipitate surface. In all cases further measurement is necessary to explain the mechanism of the impact of the surfactant.

The Langmuir adsorption theory is based on adsorption of gases and it is not apparently valid without any differences for adsorption from the solutions. Thus, the experimentally obtained data were also analyzed in terms of non-linear regression. Four adsorption models (Langmuir, Freundlich, Langmuir-Freundlich and Temkin) were used and compared. The non-linear regression was calculated by means of the OPstat program using various algorithms – a genetic algorithm, simplex, and the Levenberg-Marquardt algorithm. The Akaike criterion was chosen to evaluate the experimental data correspondence with a given theory. The lowest value of Akaike criterion was found for the Langmuir model. In other words non-linear regression also confirmed the Langmuir model's applicability.

Figure 4 also shows us the noteworthy similarity of the adsorption isotherms with the changes of zeta potential of the adsorption systems. In other words the adsorption of surfactant causes a change of the surface charge. The addition of anionic surfactant causes a decrease of zeta potential adsorbents; zeta potential becomes more and more negative. The same results were found for other adsorption systems [15]-[18].

IV. CONCLUSIONS

Adsorption of selected surfactants on ferrous sediments was monitored. These materials, which represent unusable waste, show a relatively high adsorption capacity for surfactants. The adsorption process can be described by the "classic" Langmuir theory and the calculated parameters of the Langmuir equation can be used for potential specific applications. The adsorption process was studied as well with regard to changes of surface charge. Measuring proved a connection between adsorption and the change of the zeta potential of the particles. Particularly due to its adsorption capacity and price, this material ranks among many cheap adsorption materials

possibly usable to treat waste water containing surfactants.

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