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Comparison of adsorption affinity of anionic polyacrylamide for nanostructured silica-titania mixed oxides

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ABSTRACT

The anionic polyacrylamide PAM (with various contents of carboxyl groups) adsorption mechanism on the surface of SiO_2-TiO_2 (ST) mixed oxides in the pH range of 3–9 was examined. Two types of ST solids differing in their composition were applied, namely ST 20 (80% silica and 20% of titanium dioxide) and ST 80 (20% of SiO_2 and 80% of TiO_2). The adsorption affinity of anionic PAM for the mixed oxide surface was determined using UV–Vis spectrophotometry, whereas the influence of polymer presence on the solid suspension stability was specified using turbidimetry. The most probable adsorption mechanism of polyacrylamide at the solid-liquid interface was proposed additionally based on the surface charge density and zeta potential values calculated from the potentiometric titration and the electrokinetic measurements respectively. The obtained data revealed that the anionic polymer has greater adsorption affinity to the surface of silica-titania mixed oxide which contains 80% of TiO_2. For both examined oxides the PAM adsorbed amounts are higher in solutions of higher pH values and for polymeric macromolecules containing a larger number of carboxyl groups. The specific nanostructure of PAM adsorption layers formed on the ST oxides surface influences solid suspension stability (generally promoting steric or electrosteric interactions).

Contents

1. Introduction

Nowadays a great variety of adsorbents with specific structure and surface properties are applied in many fields of human activity (mainly in environmental protection, agriculture and industry) [1–10]. An important group among these materials is oxide adsorbents, such silica,

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alumina, titania and zirconia as individual as well as mixed. In addition to their good mechanical properties, they are characterized by specific surface morphology and the presence of hydroxyl groups. Depending on the solution pH value these amphoteric groups can connect or disconnect proton, causing creation of the solid surface charge. Each oxide material possesses a specific value of pH (the so-called point of zero charge) at which the numbers of positively and negatively charged hydroxyl groups on the solid surface are the same [11]. This is a very important parameter which describes directly the surface properties and adsorption affinity of applied oxide.

To design the specific surface characteristics of sorbent (required for a particular practical application), the mixed oxides were synthesized. In such a way the combination of physical and chemical properties of individual components can be obtained. Among the methods of mixed oxides synthesis the most popular are: co-precipitation, hydrothermal technique, sol-gel process, sonochemical approach and oxalate technique [12]. Additionally, different modifications of the prepared mixed oxides were performed. One of the methods requires the use of macromolecular compounds. The functional groups of the polymeric chains bound with the solid surface impart new properties of the formed composite [13–15]. In such a way the unique structure of polymer layer deposited on the mixed oxide surface can be obtained. Elastic macromolecules can assume a greater number of various conformations on the solid surface leading to formation of nano-sized polymeric film.

Our previous studies focused on the mixed oxide surface modification by the synthetic polymers with a relatively low-molecular weight. The effect of anionic poly(acrylic acid) molecular weight and solution pH in relation to the silica-alumina oxide was examined [16,17]. This type of mixed oxide (SiO_2-Al_2O_3) was also used in adsorptive removal of dyes from aqueous solutions and wastewaters [18,19]. The influence of nonionic polyvinyl alcohol adsorption on the stability of mixed alumina-silica-titania oxide suspension was studied [20,21]. Adsorption and electrokinetic properties of the other double oxides (Mg_xO_y-SiO_2, Zn_xO_y-SiO_2 and Cu_xO_y-SiO_2) in relation to polyvinyl alcohol were determined depending on the solution pH, mixed oxide composition and content of unhydrolysed acetate groups in polymeric macromolecules [22,23].

The present research concerns determination of high-molecular weight anionic polyacrylamide (PAM) impact on the stability of nanostructured silica-titania mixed oxide suspension. The specific conformation of the adsorbed macromolecules is a result of influence of many parameters, such as solution pH, polymer molecular weight, content of carboxyl groups in macromolecules and mixed oxide composition. By appropriate selection of these parameters one can obtain polymer films with the desired structure, which leads to effective control of the solid suspension stability in the polymer presence.

The anionic polyacrylamide is widely used in the flocculation process in the procedures of industrial wastewater purification and drinking water treatment. Due to the ability of long PAM chains to form polymer bridges between the solid particles, the undesirable suspended solids, polyvalent metal ions, organic compounds and microorganisms can be efficiently removed from the aqueous medium [24–26]. The other important areas of application of polyacrylamides are in agriculture as the rain erosion control agent [27] and in the oil extraction supporting processes in the enhanced oil recovery (EOR) method [28]. The additional fields of polyacrylamide usage include mining operations, mineral processing, metallurgy, papermaking industry, food processing, cosmetics production and drug delivery systems designing.

2. Experimental

2.1. Materials

Mixed fumed oxides SiO_2-TiO_2 (ST, pilot plant at the Institute of Surface Chemistry, Kalush, Ukraine) with two ratio silica/titania were used as the adsorbents. The detailed characteristics of these oxides are included in Table 1. Many properties of mixed fumed oxides were described in detail elsewhere [29–31]. According to the pyrogenic synthesis method, mixed SiO_2-TiO_2 were obtained by co-burning silicon and titanium tetrachlorides in a hydrogen oxygen flame at a temperature of 1100–1400 °C. The structure of the synthesized mixed oxides is dependent on many factors, namely the ratio of the initial components, the flame temperature, and the flow velocity. Conditions during the flame synthesis prevent the formation of large crystallites and the formation of TiOTi or SiOSi bonds may be preferable to the formation of TiOSi bonds at the surface of nuclei of some phases, especially if they tend to be crystalline. Nevertheless, the contribution of TiOSi bonds to the structure of the surface of fumed mixed oxides remains significant and its effect on adsorption and electrosurface properties can be quite appreciable. A minimum in the surface C_{Ti} value at $C_{TiO2} = 20$ wt% corresponds to the maximal number of SiOTi bridges in fumed ST [29–31] and the titania phase in ST20 consists of a major portion of anatase

Table 1
Physicochemical characteristics of applied samples of adsorbate (anionic polyacrylamide) and adsorbent (silica-titania mixed oxide).

Anionic polyacrylamide PAM		Silica-titania ST mixed oxide	
Symbol	PAM 14.0_20%	Symbol	ST 20
Weight average molecular weight [Da]	14,000,000	Composition	SiO_2: 80% TiO_2: 20%
Carboxyl groups content [%]	20	Point of zero charge	3.8
pK_a	3.7	Isoelectric point	<3
Dissociation degree [%]	pH 3: 16.6 pH 6: 99.5 pH 9: 99.9	Textural characteristics	BET surface area [m^2/g]: 84 micropore area [m^2/g]: 8.84 total pore volume [cm^3/g]: 0.255 micropore volume [cm^3/g]: 0.003 average pore diameter [nm]: 12
Anionic polyacrylamide PAM		Silica-titania ST mixed oxide	
Symbol	PAM 15.5_50%	Symbol	ST 80
Weight average molecular weight [Da]	15,500,000	Composition	SiO_2: 20% TiO_2: 80%
Carboxyl groups content [%]	50	Point of zero charge	4.8
pK_a	3.6	Isoelectric point	< 3
Dissociation degree [%]	pH 3: 20.1 pH 6: 99.6 pH 9: 99.9	Textural characteristics	BET surface area [m^2/g]: 22 micropore area [m^2/g]: 6.7 total pore volume [cm^3/g]: 0.0609 micropore volume [cm^3/g]: 0.0029 average pore diameter [nm]: 11