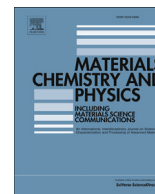




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Investigations of the properties of the manganese dioxide suspensions in the presence of guar gum and carboxymethylcellulose

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H I G H L I G H T S

- Carboxymethylcellulose and guar gum can be used as stabilizers of MnO₂.
- The adsorption of carboxymethylcellulose on MnO₂ is higher than guar gum.
- The adsorption of carboxymethylcellulose on MnO₂ effects the electric double layer.
- The adsorption of guar gum on MnO₂ influences the zeta potential.

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Properties of manganese dioxide suspensions in the presence of two polysaccharides: non-ionic guar gum (GG) and anionic carboxymethylcellulose (CMC) were investigated using NaCl as a background electrolyte. The colloidal stability of MnO₂ suspensions in the presence and absence of these two polymers was measured. It was found that both polymers improve stability of measured suspensions. This fact results from steric stabilization (low polymer concentrations) and depletion stabilization (high polymer concentrations) for MnO₂ particles covered with macromolecules. Next the kinetics of the adsorption of these two polymers on MnO₂ as well as the heats of GG and CMC adsorption processes were measured. The obtained data proved that CMC is adsorbed more effectively on the manganese dioxide surface than guar gum. To obtain more information about the changes of adsorption of these polymers on MnO₂ some factors influencing this process (pH, ionic strength of the background electrolyte) were investigated. The data obtained from the surface charge density and the zeta potential measurements allowed the analysis of the structure of the electric double layer created by polymers on the solid surface.

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1. Introduction

Controlling of stability and flocculation of colloidal dispersions is crucial for many branches of industry including food, cosmetics, pharmaceutical, chemical, sewage and mining industries [1]. There are two basic types of interactions in the colloidal systems that are responsible for stabilization–flocculation processes: the first one is attractive forces (van der Waals) and the other is the repulsive ones. When the attraction forces (caused by permanent dipole–permanent dipole interactions (Keesom), the permanent dipole–induced dipole forces (Debye) and transitory dipole–transitory dipole forces (London)) are stronger than repulsive forces the particles of

the solid adhere with each other and the consequence of that is flocculation [2]. The stability may be obtained for example by the addition of polymer to the colloidal suspensions. It must be emphasized that the addition of high molecular weight substance to the colloidal dispersion can cause either stability or flocculation depending on molar mass of the adopted polymer, its chemical character and concentration. Because of their biodegradability and nontoxicity polysaccharides are very often used as the additives influencing the properties of suspensions. They find application not only as stabilizers or flocculants, but also as emulsifiers, thickeners and binders [3,4]. The practical use of polymers as the above-mentioned additives to the colloidal suspensions requires many experimental investigations. Among them the most important are the determination of the polymer adsorption onto the solid surface as well as the mechanism of this process, the estimation of the conformation of the polymers at the interface and also the

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determination of the elektrokinetic properties of these systems. However, despite many attempts, the mechanism of polysaccharides adsorption on the solid surfaces has not been fully explained which reduces their possible applications. It is generally accepted that the adsorption of polysaccharides at the metal oxide surface results from the reaction between the hydroxyl groups of polymer macromolecules and metal hydroxyl groups present on the mineral surface. According to one group of scientists the hydrogen bonding is the primary adsorption mechanisms [5,6] but according to others the acid–base reaction is crucial [7–9]. The other possible mechanisms of ionic polysaccharides adsorption that also should be taken into account are electrostatic interactions.

In this paper the influence of two polysaccharides: carboxymethylcellulose (CMC) and guar gum (GG) on the properties of manganese dioxide suspensions was discussed. Carboxymethylcellulose is an anionic polysaccharide. Parolis et al. [10] noticed that calcium and magnesium ions increased the CMC adsorption in comparison to monovalent cations onto talc thus promoting the dispersion of talc by CMC. They also found out that at the ionic strengths less than $10^{-1} \text{ mol dm}^{-3}$ divalent cations caused greater coiling of CMC chains, but at the ionic strength higher than $10^{-1} \text{ mol dm}^{-3}$ the coiling effect was equivalent between divalent and monovalent cations. However, the CMC adsorption on talc was still greater in the presence of Ca^{2+} and Mg^{2+} suggesting a specific interaction between the mineral surface, the divalent cations and CMC, which did not occur with K^{+} ions. Bacchin et al. [11] studied the adsorption of different molar masses of CMC onto talc. They found out that the presence of CMC improves the dispersion of talc by avoiding foam and aggregate formation. Khraishah et al. [12] also studied the effect of molecular weight and concentration on the adsorption of CMC onto talc but the measurements were performed at different ionic strengths. The results showed that the increasing molecular weight of CMC results in the increase of CMC adsorption on talc as well as the increase of electrolyte ionic strength. Wang and Somasundaran [13] measured the adsorption of CMC on talc using adsorption, electrophoretic mobility measurements, FTIR, fluorescence spectroscopy, AFM as well as molecular modelling. According to their results, the adsorption of CMC on talc is affected by pH and ionic strength, which indicates the important role of electrostatic force in adsorption. The main driving forces responsible for CMC adsorption on talc are combination of electrostatic interactions and hydrogen bonding. Pawlik et al. [14] studied the adsorption of CMC from the electrolyte solution (NaCl , KCl) of different ionic strength onto illite and dolomite. According to them the increase of adsorption accompanying the increase of ionic strength, which is due to the fact that the CMC macromolecules coil in solution to an extent that depends on electrolyte concentration. Shortridge and co-workers [15] studied the effect of chemical composition and molecular weight of CMC and modified guar gum reagents on the flotation of talc. They found out that guar was much more effective depressants of talc than the CMC samples when $0.001 \text{ mol dm}^{-3} \text{ KNO}_3$ was used as the background electrolyte. The second polymer used in this study is non-ionic guar gum. The mechanism of adsorption of this polymer is not fully understood. The hydrophobic interactions were suggested for guar gum adsorption onto talc by Steenberg and Harris [5] and Jenkins and Ralston [16]. On the other hand, Rath and Subramanian [17], Jucker et al. [18] and Ma and Pawlik [19,20] proposed that hydrogen bonding and chemical interactions between macromolecules of guar gum and the surface of the adsorbent are the main driving force in this process. This observation was confirmed by Wang and Somasundaran [13] who found the decrease in guar gum adsorption onto the talc surface in the presence of urea, which is a hydrogen bond breaker. Due to the fact that the adsorption of guar gum is not affected by ionic

strength, the authors also concluded that hydrogen bonding is responsible for guar gum adsorption onto talc. A very interesting conclusion was drawn by Bicak and co-workers [21]. They found out that at low pH values the dominant mechanism of guar gum adsorption on pyrite is hydrogen bonding, but with the alkaline pH values the mechanism that can be postulated is the acid–base reaction with the effect of iron oxy/hydroxyl ions present at pH 9 and 11.

The aim of the presented studies was to compare and correlate the adsorption of polysaccharides (GG, CMC) on the MnO_2 surface with the colloidal stability and elektrokinetic properties of these systems. The information was obtained within three the above-mentioned areas in order to get a more complete description of the polysaccharide/ MnO_2 dispersions.

Guar gum is a natural, nonionic, non-toxic and biodegradable polysaccharide. It is produced from the seeds of the two annual leguminous plants, *Cyamopsis tetragonalobus* and *Cyamopsis psoraloides* [19]. The functional polysaccharide in guar gum is guaran. It contains the units of β -D-mannopyranose with α -D-galactopyranose ones linked with the position (1 \rightarrow 4) and connected to the mannose backbone through (1 \rightarrow 6) glycosidic linkages. The polymannose is randomly substituted with galactose. The degree of substitution of polymannose varies from 1.0 to 1.8 [20]. Because of the random nature of this substitution, the least substituted sections of the guar gum show the greatest tendency to associate, while the more densely substituted regions serve to solubilize the polymer chains [19].

Sodium salt of carboxymethyl ether of cellulose, anionic, biodegradable polysaccharide is produced from cellulose, monochloroacetic acid and sodium hydroxide. The maximal, theoretical value of its DS – degree of substitution (the average number of carboxymethyl groups per anhydroglucose unit) is 3, but for the commercial samples of CMC it is usually from 0.5 to 1.5 [12]. The degree of substitution of CMC used in the present measurements equalled 0.75. Each CMC unit contains $-\text{CH}_2\text{COO}^-$ and $-\text{OH}$ groups enabling formation of hydrogen bonds. The example formula of CMC is presented in Table 1.

The chemical inertness, stability in a broad pH range and well-defined interface allow to use MnO_2 in many adsorption processes. This compound occurs in nature as a mineral pyrolusite and forms a few polymorphic modifications (α , β , γ). MnO_2 finds application in many branches of industry for example in the production of matches, in glass-making industry for decolourization of glass and as a depolarizer in voltaic cells [22]. Because the above-mentioned reasons this compound was chose as the adsorbent.

2. Experimental

2.1. Materials

MnO_2 produced by POCh Gliwice (Poland) was used as an adsorbent. This chemical compound is one of the most stable manganese (IV) compounds. The BET specific surface area for the sample was found to be $35 \text{ m}^2 \text{ g}^{-1}$. The particle size distribution of the MnO_2 sample determined with the use of a Malvern Mastersizer 2000, fell entirely in the range from $1.82 \mu\text{m}$ to $22.71 \mu\text{m}$, with a volume average size of $6.78 \mu\text{m}$. The adsorbent was washed with doubly-distilled water until the conductivity of the supernatant was smaller than $2 \mu\text{S cm}^{-1}$. The XRD measurements confirmed that MnO_2 was free of impurities.

Guar gum was obtained from Sigma–Aldrich. All guar gum stock solutions were prepared by quick addition of 0.045 g of gum powder into 45 cm^3 of vigorously stirred water and further stirring for 30 min. The solution was refrigerated overnight to ensure complete hydration or dissolution of guar gum and then filtered

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