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Research article

Lysozyme as a flocculant-inducing agent improving the silica removal from aqueous solutions - A turbidimetric study

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ABSTRACT

In this paper, the lysozyme (LSZ) adsorption impact on the silica suspension stability was established. In other words, the stabilization/destabilization mechanism of the SiO_2/LSZ system was explained based on the adsorption, electrokinetic and stability measurement results. Lysozyme adsorbs on the silica surface in the whole pH range. This process contributes to the changes in silica surface charge and zeta potential values. The lysozyme addition influences the system stability too. At pH 7.6 and 9, a large decrease in the silica suspension stability was found. It is connected with the neutralization of solid negative charge by the positively charged macromolecules. As a result, large aggregates can be formed, which is highly desirable in the silica removal procedure.

1. Introduction

Lysozyme (LSZ) is an enzymatic protein with antibacterial properties. It hydrolyses the β-1,4-glycosidic linkage between N-acetylglucosamine and N-acetylmuramine acid in the bacteria cell wall. This protein is a component of tears, saliva and other tissue fluids. LSZ is used in many industries, including the food and pharmaceutical ones (Panfil-Kuncewicz, 1988; Wang et al., 2005). Nowadays, lysozyme is an object of various scientific research. Many of them relates to the lysozyme use in drug delivery (Haselberg et al., 2011; Cai and Yao, 2013).

The LSZ adsorption on the silica surface is well-documented. Rezwan et al. (2005a) described the influence of the solid surface charge on the protein adsorption mechanism. They clarified the conditions, under those the lysozyme and bovine serum albumin adsorb on the silica particles. Steri et al. (2013) examined the ionic strength effect on the LSZ adsorption/desorption amount on the SBA-15 mesoporous silica. Czeslik and Winter (2011) explained the temperature input on the lysozyme macromolecules conformation adsorbed on the SiO_2 particles. Kumar et al. (2014) presented pH-dependent interaction and resultant structure of silica particles and lysozyme macromolecules. Rimola et al. (2013) described SiO_2 surface features and their role in the biomolecule adsorption using computational and experimental methods. Bharti et al. (2014) focused on bridging interactions protein-silica as a function of pH, ionic strength and protein concentration. In turn, Su et al. (1988) studied the silica-water interface with the LSZ macromolecules adsorbed using neutron reflection.

On the other hand, the lysozyme adsorption effect on the suspension stability as a function of pH value is scarcely described in the literature. Therefore, this paper focused on this subject. It presents the probable stabilization/destabilization mechanism of the silica suspension in the LSZ presence. The measurements were performed using a turbidimeter, which determines the system stability precisely. The explanation of the LSZ adsorption effect on the SiO_2 suspension stability is not possible without adsorption amount and electrokinetic studies and, due to this fact, this paper described also these experiments. The presented information on SiO_2/LSZ system stability may be valuable in the environmental engineering. In water purification procedure proteins may act as flocculant-inducing agents (Santiago et al., 2002).

Coagulation is generally the first process in the water and wastewater purification procedure. Including oxidation and sedimentation, it is the most important step in this technology. Coagulation is based on the colloidal system destabilization, which decreases the dispersion degree (Adamski, 2002). This process occurs after the coagulant addition, immediately. It reduces the electrokinetic potential and thereby weakens the repulsive forces acting between colloidal particles. The most effective coagulation is possible when the zeta potential approaches or is equal to zero (Magrel, 2000). Aluminum and iron salts are commonly used coagulates. After their hydrolysis, they form hydroxides neutralizing the impurity charge. However, due to the slow rate of the process, the polyelectrolytes or flocculant-inducing agents must be added to the system (Santiago et al., 2002; Sanchez-Martin et al., 2012). These substances initiate flocculation, i.e. the

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agglomeration of destabilized particles in the macromolecular compound presence (Adamski, 2002; Wiśniewska et al., 2018a). Polyelectrolytes may be also helpful in metal acquisition from geothermal water (Wiśniewska et al., 2018b).

Looking for new flocculants is a significant issue due to drinking water lack in many regions. Taking this into account, this paper described lysozyme as potential agent improving flocculation. It defines the pH value, at which the aqueous silica suspension is the most destabilized after the LSZ addition. The silica removal from aqueous solutions is essential because it is a very common mineral on the Earth's sphere that occurs also in surface waters. In addition, silica is widely used in the industry (glass and construction), so its presence in the sewage is inevitable. The silica removal from aqueous solutions is examined by many researchers. Hermosilla et al. (2012) focused on the coagulation and reverse-osmosis of SiO_2 particles present in effluents from recovered-paper mills. Miranda et al. (2015) described the silica coagulation with aluminum salt in the suspended solids presence. These researchers claimed that silica is one of the most important substances that accumulate in papermaking water cycles. Den and Wang (2008) stressed that SiO_2 makes desalination difficult. Thus, they used electrocoagulation pretreatment in silica removal from brackish water. Emamjomeh and Sivakumar (2009) summarized the pollutants that may be removed by electrocoagulation and electrocoagulation/flotation processes. Therefore, the presented subject may be considered as a very important and actual. Our previous study described another potential flocculant-inducing agent. It was related to the chromium(III) oxide removal in the albumin presence (Szewczuk-Karpisz and Wiśniewska, 2014).

2. Experimental

2.1. Materials

Silicon(IV) dioxide (silica, SiO_2), delivered by *Sigma-Aldrich,* was used in the experiments. This is a finely crystalline, white solid with porous structure. Using the BET equation (Brunauer et al., 1938) and nitrogen adsorption/desorption isotherm method (*ASAP 2405* analyzer. *Micrometritics*) the SiO_2 average pore size and specific surface area were determined. The first parameter was equal to 11.3 nm which means that silica is a mesoporous material. In turn, the SiO_2 specific surface area was 145 m^2/g. The crystalline structure of the solid was determined using X-ray diffractometer (*Empyrean, PANalytical*). The obtained XRD pattern is shown in Fig. 1. The mean particle size was also measured (zetameter *Zetasizer 3000, Malvern Instruments*); it was equal to 225 nm. Porous and crystalline silica was chosen for experiments due to its wide application in industry.

Lysozyme (LSZ), delivered by *Sigma-Aldrich* (62971, Poland), isolated from chicken egg white, was also used in the study. According to literature, the LSZ molecular weight is 14.3 kDa and the isoelectric point (pI) is about 11. The LSZ macromolecule is composed of 128 amino acids (Watter, 1951). Lysozyme has a high internal stability, i.e. its structure is not highly dependent on the solution pH value. In the pH range from 1 to 8 its structure remains unchanged (Ogasahara and Hamagichi, 1967).

2.2. Methods

All measurements were performed at room temperature, i.e. 25 °C. As a supporting electrolyte 0.01 M NaCl was used. The experiments were carried out as a function of pH value (3–9). The lysozyme concentration is expressed in 'ppm' (parts per million), which is equivalent to 'mg/l' (weight concentration).

2.2.1. Viscosity measurements

Viscosity measurements were used for the hydrodynamic radius (r_h) determination of the lysozyme macromolecules at various pH values. The LSZ concentration was in the range of 10–500 ppm. The measured viscosity (η) was converted to the relative viscosity (η_r) and the intrinsic viscosity $[\eta]$ using the equations (Porejko et al., 1965):

$$\eta_r = \frac{\eta}{\eta_s} \tag{1}$$

$$[\eta] = \lim_{c\to 0}\left(\frac{\eta_r - 1}{c}\right) = \lim_{c\to 0}\left(\frac{\eta_{sp}}{c}\right) \tag{2}$$

where: c – the protein concentration, η – the EPS solution viscosity, η_r – the relative viscosity, η_s – the solvent viscosity, η_{sp} – the specific viscosity, $[\eta]$ – the intrinsic viscosity.

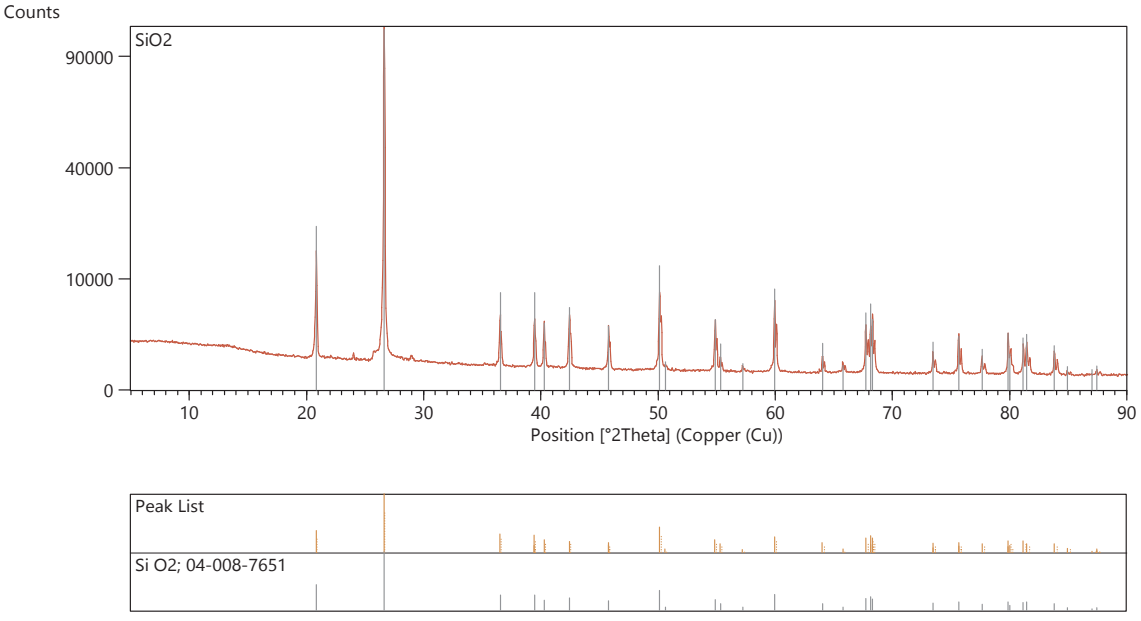

Fig. 1. Diffractogram of the SiO_2 sample with matched phases from the ICDD PDF4 + 2016 diffraction database.