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Adsorption of cationic polyacrylamide on the surface of mesoporous nanozirconia and its influence on the solid aqueous suspension stability

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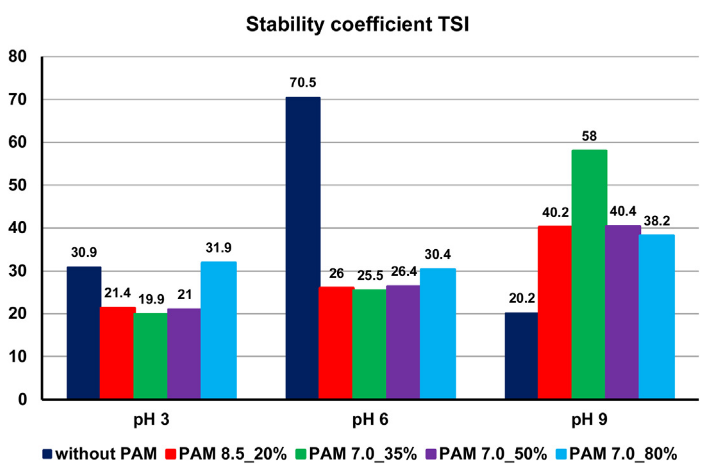
HIGHLIGHTS

- Cationic PAM adsorption mechanism on zirconium(IV) oxide was examined.
- Mesoporous (pore diameter 31 nm) nanozirconia (grain size 100 nm) powder was used as adsorbent.
- Spectrophotometry, microelectrophoresis, turbidimetry and potentiometric titration were applied.
- Cationic groups content in PAM chains affects stability properties of zirconia suspension.
- PAM shows the greatest adsorption on ZrO_2 surface at pH 9.

GRAPHICAL ABSTRACT

Stability coefficients TSI obtained for ZrO_2 suspensions without and with PAM.



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ABSTRACT

The adsorption mechanism of cationic polyacrylamide (PAM) on the mesoporous nanozirconia was studied. The effects of solution pH (in the range 3–10) and cationic groups content (20–80%) in the polymeric chains were examined. The influence of polymer adsorption on both the structure of electrical double layer and stability of aqueous ZrO_2 suspension was determined. It was shown that the porosity of zirconia (mean pore diameter 31 nm) has the greatest impact on the PAM adsorption level at pH 9, at which molecules can penetrate into the pores. As a result, the greatest amount of adsorbed polyacrylamide was obtained. The specific conformation of adsorbed macromolecules (containing positively charged cationic groups) is responsible for the observed decrease of the solid surface charge density and increase of the zeta potential of nanozirconia particles. Polyacrylamide has the greatest impact on the ZrO_2 suspension stability at pH 6 (significant improvement of the system stability due to electrosteric interactions).

1. Introduction

Polyacrylamides (both neutral and ionic) – PAMs, are widely used in many fields of human activity [1–8] owning to their good

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water solubility, non-toxicity, relatively low price and biodegradability. The most important of PAM applications are: as effective flocculents in wastewater purification, in oil extraction supporting processes (high viscosity of PAM solution), in control of rain erosion of agricultural soils (improvement of soil consistency, increase in its aeration, porosity and viscosity, as well as reduction of sediments transport), as fertilizers in gardening suitable for arable land (significant improvement of vigour, colour, rooting depth and seeds formation, while simultaneously reducing water consumption, elimination of disease and cultivation costs).

Most practical applications of polyacrylamide are associated with its adsorption on the solid surface. Adsorption occurs commonly in many areas of human life – biological, environmental and industrial [9–18]. It should be noted that the adsorption process of macromolecular compounds is extremely complicated and dependent on many factors. The ability of the polymer chains to assume a huge number of the conformation at the solid – liquid interface is the main reason for the high complexity of this problem description. Therefore, understanding the mechanism of adsorbate connection with surface sites of the metal oxide is essential not only for the practical applications of this type of systems, but it also has great cognitive importance.

In the present study zirconium(IV) oxide was used as the adsorbent. Its physicochemical characteristics indicate that both the pore size (31 nm, mesopores) and the particle diameter (100 nm, nanopowder) is in the range of nanotechnology interest. Mesoporous structure of the adsorbent promotes the adsorption of macromolecules inside them, which can significantly increase the amount of polymer bound to the solid surface. In addition, zirconium(IV) oxide is characterized by the well-defined solid – solution interface, has high stability and minimal solubility in the wide pH range. Due to these properties it satisfies the requirements for good adsorbents and can be used as a model system which will allow to get to know the mechanisms of interactions of cationic polyacrylamide with the surface hydroxyl groups of the metal oxide. Additionally, there are very few reports in the scientific literature concerning cationic PAM influence on the adsorption, electrokinetic and stability properties of aqueous metal oxide suspension [19–21]. Most of them refer to the anionic forms of polyacrylamide. For this reason the presented results can complete knowledge in this scientific area.

It should be noted that ZrO_2 can be practically applied, mainly as a ceramic material in dental prosthetics and preparation of various implants. Its possible use in this field of medicine depends on both its physicochemical properties (high mechanical strength and chemical resistance) and excellent biocompatibility with human body tissues [22–25]. The other applications of zirconium(IV) oxide include: pigments, catalysts or catalysts carrier. These applications require determination of zirconia adsorption properties in relation to various substances, including also polymers.

2. Experimental

2.1. Materials

Zirconium(IV) oxide (*Sigma-Aldrich*), was used as an adsorbent. This metal oxide has monoclinic crystal structure and purity above 99%. Its average pore size – about 31 nm – is in the range of mesopores. The specific surface area of this adsorbent is 21.7 m^2/g and the average particle size is equal to about 100 nm (nanosize). The adsorbent pore diameter and surface area were determined on the basis of the BET method using the ASAP 2405 analyzer (*Micrometritics*). The particle size was specified using a Mastersizer 2000 (*Malvern Instruments*). The detailed information concerning particle size determination was described in our previous paper [26]. On the other hand, the TEM image of nanozirconia is available on the producer website.

Four samples of cationic polyacrylamide – PAM (*Korona*) differing in cationic group contents were applied. These groups contain the quaternary amine fragments which are the source of positive charges in polymer macromolecules. The polydispersity index (PDI) of used PAM samples does not exceed value 1.4. The detailed characteristics of the polymer samples are presented in Table 1.

The sodium chloride solution of the concentration $1 \cdot 10^{-2}$ mol/dm^3 was used as a supporting electrolyte. All experiments were carried out at 25 °C.

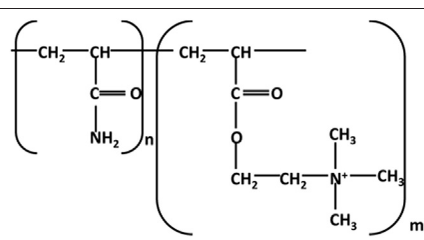
2.2. Methods

2.2.1. Adsorption measurements

The adsorption measurements were performed with the static method in the PAM concentration range 5–120 ppm using 0.07 g of the solid. Three series of suspensions were prepared – for each of them the appropriate pH was adjusted, i.e.: 3, 6 or 9 ± 0.1 (pH-meter, *Beckman Instruments*). Then, the suspensions were shaken in a thermostated water bath for 24 h (shaker Unimax 1010, *Heidolph*) at temperature 25 °C, meanwhile the pH was checked. This device provides a continuous temperature control, which is maintained at a constant level. After this time, the solid was centrifuged (MPW, *Med. Instruments*) and 5 cm^3 of supernatant was taken for polymer concentration determination. The blue complex formation as a result of the reaction of cationic polyacrylamide with a saturated solution of bromine, sodium formate and starch (in acetate buffer) [27] was observed. The absorbance of polymer solution was mea-

Table 1
Characteristics of cationic polyacrylamide samples.

Chemical formula



Symbol		PAM 8.5_20%	PAM 7.0_35%	PAM 7.0_50%	PAM 7.0_80%
Molecular weight [Da]		8 500 000	7 000 000	7 000 000	7 000 000
Cationicity in mole [%]		20	35	50	80
pK_b		10.1	10.1	9.9	9.9
α [%]	pH 3	99.9	99.9	99.9	99.9
	pH 6	99.9	99.9	99.9	99.9
	pH 9	92.6	92.6	88.8	88.8