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Research article

Cationic polyelectrolyte induced separation of some inorganic contaminants and their mixture (zirconium silicate, kaolin, K-feldspar, zinc oxide) as well as of the paraffin oil from water

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ABSTRACT

The flocculation efficiency of a cationic polyelectrolyte with quaternary ammonium salt groups in the backbone, namely PCA5 was evaluated on zirconium silicate (kreutzonit), kaolin, K- feldspar and zinc oxide (ZnO) suspensions prepared either with each pollutant or with their mixture. The effect of several parameters such as settling time, polymer dose and the pollutant type on the separation efficacy was evaluated and followed by optical density and zeta potential measurements. Except for ZnO, the interactions between PCA5 and suspended particles led to low residual turbidity values (around 4% for kreutzonit, 5% for kaolin and 8% for K-feldspar) as well as to the reduction of flocs settling time (from 1200 min to 30 min and 120 min in case of kaolinit and K-feldspar, respectively), that meant a high efficiency in their separation. The negative value of the zeta potential and flocs size measurements, at the optimum polymer dose, point to contribution from charge patch mechanism for the particles flocculation. A good efficiency of PCA5 in separation of paraffin oil (a minimum residual turbidity of 9.8%) has been also found.

1. Introduction

The increased environmental pollution caused by various industrial activities and natural events leads to a deterioration of the water quality and requires the removal of a variety of pollutants from the surface, household (domestic) and industrial wastewaters. One way to reduce the amount of dissolved and colloidal contaminants is the addition of charged polymers. Taking into account that a great part of pollutants found in water (clays, metal ions/oxides, detergents, dyes, oils, greases, etc.) are negatively charged, cationic polyelectrolytes (synthetic and natural) are commonly used in the suspension/emulsion separation processes due to their ability to attach strongly to charged particles via electrostatic attractions (Nasser and James, 2006; Bratskaya et al., 2006; Szygula et al., 2009; Ghimici et al., 2009a, 2010; Ghimici and Nichifor, 2010, 2012, 2013; Tian et al., 2010; Liimatainen et al., 2011; Zhang et al., 2013; Zhao et al., 2013; Prado and Matulewicz, 2014). Weak cationic polyelectrolytes are not fully charged in solution and their charge can be modified by changing the solution pH, while strong polyelectrolytes dissociate completely in solution, irrespective of the pH values. In order to avoid the pH adjustment, polyelectrolytes bearing quaternary ammonium salts groups (either in the side or main chain) are preferred. They can be synthesized by homopolymerization/copolymerization of charged monomers (such as homopolymers and copolymers of aminoalkylacrylates), modification of some polymers (such as alkylation of polymers containing tertiary amine groups), polycondensation of epichlorohydrin with dimethylamine (Huang and Lipp, 1996). Cationic polyelectrolytes having different contents of (N,N-dimethyl-2-hydroxypropylenammonium chloride) groups located along the main chain, without or with nonpolar side chain were synthesized by polycondensation of epichlorohydrin (ECH) with dimethylamine (DMA) and N, N-dimethyl-1, 3-diaminopropane (DMDAP) – polymer PCA5, and primary amines with non-polar chains (hexyloxypropylamine - polycation PCA5H and decyloxypropylamine - polycation PCA5D (Dragan and Ghimici, 1991, 1998). The viscometric and conductometric behavior of these compounds in dilute and semidilute aqueous solutions in the presence or absence of low molar mass salts as well as in solvent mixtures of water/methanol and water/acetone have given information about the conformational changes of the above mentioned polymer chains in different media (Ghimici et al., 1997; Dragan and Ghimici, 2001, 2002;

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Dragan et al., 2004; Ghimici et al., 2009b). Their thermal stability was also investigated (Dragan et al., 1998). As regards the possible applications, our previously published results indicated these polymers and their complexes with polyanions and/or dyes as promising flocculants in aqueous montmorillonite and dyes suspensions (Dragan et al., 1999, 2002). These investigations were performed on model suspensions containing only one pollutant. But in the real wastewaters, mixtures of different particles are usually found. Therefore, this study is focused on the flocculation efficiency evaluation of one of the above cationic polyelectrolyte, namely PCA5 on the separation of some suspensions prepared either with each pollutant (zirconium silicate (kreutzonit), kaolin, K- feldspar and zinc oxide (ZnO)) or with their mixture. The definitions of the abbreviations of this polycation are as follows: PC - polycation; A - asymmetrical diamine; the number means mole percent of the polyfunctional amine. As regards the inorganic particles, they are used in the ceramic industry for the glaze as well as the sprocket gypsie preparation and could be present in the ceramic wastewaters which have to be treated in order to be reused/recycled. The simultaneous removal of these inorganic particles with cationic polyelectrolytes was not reported so far. Moreover, from the literature reports it seems there are no systematic data concerning the removal of kreutzonit, K-feldspar and ZnO particles by synthetic cationic polymers. In addition, the efficiency of PCA5 in separation of paraffin oil was investigated. Paraffin oil is frequently used in industry as a lubricant, in medicine and cosmetics and, therefore present in the oily waste waters.

The effects of several parameters such as settling time, polymer dose (the polymer concentration in its mixture with the particles suspension) and the pollutant type on the separation efficiency were examined and followed by optical density and zeta potential measurements. The floc size distribution measurements at optimum polycation dose (the polycation dose where the minimum residual turbidity is obtained) as well as of the initial kreutzonit particles were also performed. Further, the surface morphology for the particles mixture before and after the treatment with polycation (optimum dose) was determined.

2. Materials and methods

2.1. Materials

2.1.1. Cationic polyelectrolyte

Cationic polyelectrolyte PCA5 was synthesized by condensation polymerization of epichlorohydrin (ECH) with a secondary amine, dimethylamine (DMA), and a polyfunctional amine, N, N-dimethyl-1,3-diaminopropane (DMDAP) (Dragan and Ghimici, 1991). The general structure is presented in Fig. 1. The polycation was carefully purified by dialysis against distilled water until the absence of Cl^- ions in the external water was achieved. The polymer was recovered by precipitation with acetone and finally purified with methanol/acetone as solvent/nonsolvent. The polycation was dried in vacuum on P_2O_5 at room temperature and then characterized by the content in ionic chlorine (determined by potentiometric titration with 0.02 N aqueous $AgNO_3$ solution) (Cl_i), total chlorine (determined by the combustion method – Schöniger technique) (Cl_t) and intrinsic viscosity ($[\eta]$) in saltless aqueous solution. Results were Cl_i 21.67%, Cl_t 22.56%, $[\eta]_{water} = 1327$ mL g^{-1} and the calculated average distance between ionic groups was b = 0.51 nm.

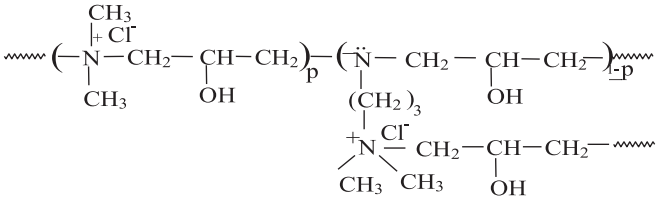

Fig. 1. General chemical structure of polycation PCA5; p = 0.95.

2.1.2. Particles

The characteristics of kreutzonit, kaolin, K-feldspar and zinc oxide particles (gift samples from Romanceram Co., Romania) used to prepare the model suspensions are shown in Table 1.

Paraffin oil was purchased by Merck company; the hydrodynamic size of the particles, Z-average (d, nm), determined by DLS measurements, was 353 nm.

2.2. Methods

The aqueous polycation solutions, stabilized at room temperature for 1 day before use as well as the inorganic particle dispersions and paraffin oil emulsion were prepared with distilled water. The concentrations of the partners involved in the systems investigated were: a) polymer solution: 1 g L^{-1} for the inorganic particle suspensions destabilization and 0.1 g L^{-1} for paraffin oil emulsion destabilization; b) inorganic particle suspensions: 0.5 g L^{-1}; c) paraffin oil: 3 g L^{-1}. The initial pH and zeta potential values of the inorganic particle suspensions and paraffin oil emulsion before treatment with polycation are also given in Table 1. In order to fully disperse the inorganic powders, the dispersions were sonicated for 15 min using an ultrasonicator (**SONICS VCX 750). Paraffin oil emulsions were also prepared by ultrasonic treatment in the pulse mode for 10 min**. The flocculation experiments were conducted in a Cole Parmer stirrer/hotplate 9 places, at room temperature. Fifty ml of the inorganic particles suspensions were placed into 100 mL glass beakers. Different volumes of polymer solutions were added at 500 rpm and stirring was continued with the same speed for about 3 min and then decreased to about 100 rpm for 15 min. After settling times established for each particles, the sample of supernatant (10 mL) was drawn out using a pipette from a depth of 0.5 cm below the surface and the turbidity was measured with a spectrophotometer SPECOL 1300 Analytik Jena at λ = 400 nm for kreutzonit, 500 nm for K-feldspar and kaolin, λ = 378 nm for ZnO. In case of paraffin oil the turbidity of subnatant (10 mL) was measured with the above mentioned spectrophotometer at λ = 400. The optimum settling time was established as the period of time where the residual turbidity decreasing was more pronounced, namely 1200 min for kreutzonit and paraffin, 30 min for kaolin, 120 min for K-feldspar and ZnO. Blank experiments were performed in the absence of polymer to evaluate "natural" separation of the suspensions and emulsion under the selected experimental conditions (pH, concentration of suspended mater). The residual turbidity (%) was expressed as percent of the initial turbidity of the particle suspensions, at time zero, in the absence of polymer. All experiments were performed in triplicate and the mean turbidity values were calculated. Standard deviation determined for the experiments was ±4%.

The zeta potential of supernatant in case of inorganic particles and subnatant in case of the paraffin oil was measured with a Zetasizer Nano-ZS, ZEN-3500 model (Malvern Instruments, Malvern, England).

Particle dimensions were measured by laser diffraction with a Mastersizer 2000 system (version 5.31) (Malvern Instruments, Malvern, England) consisting of an optical bank with a He–Ne 632 nm/2 mW laser light, a sample dispersion unit (Hydro 2000A) equipped with stirrer, a recirculation pump, ultrasonics and software to record and process results on the computer. The kreutzonit dispersion treated with a polycation dose located in the flocculation