Amphophilic Cationic Polymers as Both Flocculants and Depollutants

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Abstract

Linear and cross-linked cationic polystyrene derivatives were prepared and tested as flocculating agents towards some silica suspensions used as model of raw water. For a ratio of substitution of the aromatic ring by an alkyl ammonium group higher than 35 %, the linear polymers are water soluble and flocculate the silica suspensions according to a classical charge neutralization mechanism. The corresponding cross-linked species are very swellable gels which are also flocculants for silica but according to a different mechanism, related to heteroflocculation.

The two types of polymers can also absorb hydrophobic solutes such as polyaromatic hydrocarbons. This phenomenon is independent of the flocculation, and adsorption and flocculation may occur simultaneously. Fluorescence studies showed that this depollution effect involves the hydrophobic part of the polymers. The solute affinity for the polymer behaves like in a liquid/liquid partition and increases with the hydrophobic nature of both macromolecules and solutes.

Introduction

The production of drinking water from ground water generally involves a procedure with two separate steps: i) elimination of the particles in suspension (clay, silica, non-soluble organic matter, etc.) ii) elimination of soluble organic species which are mainly vegetal residues but may also be undesirable chemicals (micropollutants).

The first operation is mainly performed thanks to the addition of aluminium (sometimes iron) salts to the raw water. An increasing interest appears, however, for macromolecular flocculants which are very efficient and do not release aluminium ions. The second step, when necessary, is performed by adding granular or powder carbon black. Practically speaking, the two steps are not completely disconnected since aluminium derivatives lead to the formation of high specific surface mineral precipitates, so a portion of soluble organic species are removed at this stage by adsorption. In fact, this adsorption is much more efficient for humic matter than for undesirable small organic substances [1].
On the other hand, in spite of the attempts to control rejections in agriculture or industry, the number and the level of undesirable substances in raw water is increasing [2]. Powder or granular carbon black are rather expensive and must be used with care because of possible interferences with oxidizing agents or flocculants [3-5] and competitive adsorption between micropollutants and humic substances [6-9]. As for macromolecular flocculants, the compounds presently commercially available are basically very hydrophilic polymers: they are able to remove 60 to 80% of humic matter, but no interaction was found between them and small hydrophobic solutes [10-12]. Thus a more powerful class of macromolecular flocculants can be expected by selecting new water soluble polymers, preferably cationic, to ensure an easy flocculation of the mineral particles, generally negatively charged in natural water, but with a chemical structure involving hydrophobic parts which might induce the retention of micropollutants via hydrophobic interactions.

We describe here some results obtained with a series of cationic polystyrenic derivatives, some of them linear, other cross-linked, with the above mentioned structure. They were tested as flocculant of colloidal silica suspensions, considered as a very simple simulation of raw water. This flocculation was also done in the presence of polyaromatic derivatives to test the possibility of simultaneous elimination of these model pollutants. Results are analyzed in terms of hydrophobicity of the macromolecular flocculants estimated from fluorescence measurements.

**Material and Methods**

**Choice and Synthesis of the Polymer**

We showed previously that cationic polymers derived from polyacrylamide are excellent flocculants of colloidal silica [13-14]. They induce flocculation according to an electrostatic neutralization mechanism [13-15] and they can be used successfully in water treatment [16]. However we verified that they are inefficient for the retention of aromatic hydrocarbons in water. On the other hand, ion exchange resins are depicted as effective for the retention of polychlorobiphenyls and organochlorinated pesticides [17]. Between these two limit structures we expect that water soluble polymers or very swellable gels with both cationic units and hydrophobic styrenic sequences could combine the two advantageous properties of each structure.

The chemical structure of the samples prepared is schematized below where R is a hydrogen atom or an alkyl group.

Gels were synthesized in two main steps [18]. First polystyrene was cross-linked with dichloromethylbenzene according to a double aromatic electrophilic substitution [19, 20]. Quaternization was based upon a modified Tscherniak-Einhorn reaction [21-23] adapted to our polystyrenic substrate [18]. For some samples anionic gels were prepared by substituting the quaternization step by