

ON THE TYPES OF BOND DEVELOPING BETWEEN THE ALUMINIUM AND IRON (III) HYDROXIDES AND ORGANIC SUBSTANCES

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ABSTRACT

During the coagulation-flocculation processes involved in the treatment of surface waters, dissolved organics are also incorporated into the aluminium and iron (III) hydroxide flocs. A part of the dissolved organics can thus be removed by simple solid-liquid phase separation techniques, like sedimentation, flotation, sand filtration. According to laboratory evidence, durable bonds between the coagulant, or the metal hydroxides thereof, develop only over the extremely short (a few seconds) period which elapses from the formation of the metal hydroxides to the intense aggregation of the metal hydroxide sols. The bonds between these latter and the organic substances are mainly of the hydrogen bridge type, but other secondary chemical bonds and adsorption are also involved. Owing to the chemical structure and relatively low concentration levels of the organic substances, direct valence chemical bonds between the coagulants or the metal hydroxides thereof and the organic substances develop to a slight extent only.

KEYWORDS

Coagulation, flocculation, organic matter, dissolved organics removal, hydrogen bonds, valence bonds, coagulant, aluminium hydroxides.

INTRODUCTION

The basic objective of the coagulation-flocculation processes applied in water treatment is to make the solid particles of the colloidal, quasi-colloidal dispersion, and further some of the dissolved organic substances accessible to the physical processes (sedimentation, flotation, sand filtration) of solid-liquid

phase separation operations. The introduction of chemicals triggering the coagulation-flocculation processes was made necessary by the failure of the physical operations of conventional solid-liquid phase separation to remove the solid particles of the aforementioned dispersions from the water.

The metal hydroxides formed of the coagulant aluminium and /or iron(III) salts enter into firm bonds with some of the dissolved organics, making these dissolved substances suited to being removed from the water by the application of the simple physical processes of solid-liquid phase separation (sedimentation, flotation, sand filtration). The removal of dissolved organics during the coagulation-flocculation processes is substantially a "by-product" of the technologies developed for removing the solid particles of the colloidal, quasi-colloidal dispersion.

In Hungary, owing to the quality of the surface waters - which is a function of the hydrogeological conditions - attention was focused up to the mid-seventies on the removal of suspended solids by the solid-liquid phase separation methods. However, in the surface waters originating from catchments with hydrogeological conditions (forested, marshy) other than those prevailing here, the most important goal of conventional solid-liquid phase separation is the removal of organics, specifically the dissolved organics, rather than that of the suspended solids.

THEORETICAL CONSIDERATIONS

Earlier studies - with results consistent with those reported in the professional literature on the subject - have revealed the optimal conditions of solids removal and organics removal to differ widely from each other. Thus e.g. suspended solids are removed most effectively in the 6.0-6.5 pH range, whereas the optimal pH range of organics removal is 5.3-5.7. The metal hydroxides formed of the coagulant depend in their type strongly on the pH. Consequently, the metal hydroxides showing the best performance in the removal of suspended solids are not identical with those by which the dissolved organics are removed most effectively.

It is of interest to clarify what types of organics become accessible in the course of coagulation-flocculation to removal by solid-liquid phase separation. From the data published in the literature it is concluded that the substances with polar properties and particularly the compounds including the -OH or -COOH groups respond best to coagulation-flocculation treatment. The flocculants commonly used in water works technology are normally rich in -OH, -COOH, -NH and -NH₂ groups. The flocculants are known to rely for their activity on the close bonds developed with the metal hydroxides to which the coagulants are hydrolized. Remembering that the metal hydroxides, too, contain large amounts of -OH groups, it is concluded that for establishing the metal-hydroxide to organic substance bond, the latter must contain an element of high electron negative properties. This is conducive to the development of intramolecular hydrogen bonds, the strength of which attains about 10 per cent of the valence bonds.

Along with the hydrogen bonds, the electrostatic interactions play also important roles. The strong bond between the flocculant organic polymers and the metal hydroxides is due also to the fact that the functional groups of the macro-molecules forming a large part of the flocculants are hydrolized in a way to lend a resultant negative charge to the macro-molecule. The various humic and lignine substances carry also a resultant negative charge.

The data reported in the literature, as well as those obtained here, confirm that the dissolved coagulant changes within a few seconds upon addition into very poorly water-soluble metal hydroxides. The chemical reactions in which the aluminium or iron(III) salts take part take some fractions of a second, but certainly not more than a few seconds, to complete. This brief period of time is believed to be inadequate for the different types of organic compound to enter into valence bonds with the aluminium or iron(III) hydroxides. Once the chemical reactions are completed, there is little chance for the solid, thermodynamically more or less stable metal hydroxides to establish valence bonds with the functional groups of the dissolved organics. Opportunities remain, however, for the development of hydrogen bonds, electrostatic interactions and various surface interactions (adsorption), but only for a limited period of time that is not longer than a few seconds. The period of potential bonding between the organics and the metal hydroxides is limited by the fact that the metal hydroxide sols, too, aggregate, within the order of seconds, their specific surface and as a corollary their adsorption and hydrogen bonding potential decreasing rapidly.

EXPERIMENTS

In laboratory experiments cellulose-mill sulphite liquor was added to Danube water to produce a raw water with a relatively high (dissolved) organic content. The coagulant and the organic substance were added in alternating orders. The experimental data revealed positively that at identical coagulant feed rates the organic substance was removed at significantly higher efficiencies when the organic substance was present in the model system at the instant when the hydrolysis of the coagulant into metal hydroxides took place. The organics were removed at appreciably lower rates when relatively large metal hydroxide flocs were alone available for combination (Fig.1.). From these data the conclusion was arrived at that the establishment of adsorption and hydrogen bonding depends strongly on the time elapsed from the development of the metal hydroxides.

RESULTS AND DISCUSSION

Earlier studies have led to the conclusion that in raw waters of adequate buffering capacity the dissolved aluminium compounds added as coagulants transform into poorly water soluble aluminium hydroxides most effectively in the 5.7-7.5 pH range. The aluminium hydroxides mostly capable of changing the negative electric charge of the colloidal suspended solids are formed in the 6.0-6.5 pH range. On the other hand, the aluminium hydroxide species which are stable in the 5.3-5.7 pH range remove organics at the highest efficiency. In this pH range about 90 % of the Al-compounds added as coagulant are transformed into poorly water soluble Al-hydroxides, the remaining 10 % being present in the form of readily soluble Al-compounds (hydroxides). In accordance with the conditions of dynamic equilibrium, the transition between the solid and liquid aluminium hydroxide phases is a continuous, reversible one.

It should be remembered that solid-liquid phase separation techniques will remove the organic matter alone which has been incorporated during the coagulation-flocculation processes into the aluminium- or iron(III) hydroxide flocs. From the optimal pH range of organics removal and the measurement data illustrated in Fig.1, it seems safe to conclude that the organic substances enter into durable bonds with the aluminium hydroxide species which are still dissolved, but are transformed by polymerization

processes within a short period of time (of a few seconds order) into solid forms. In view of the fact that in the development of bonds (dissolved) aluminium hydroxides are involved, valence bonds have little chance of developing, but bonds of the hydrogen-bridge type are highly probable.

As will be perceived from the data shown in Fig.1., the adsorption or electrostatic bonds into which the positively charged aluminium-hydroxide sols (or aggregates, floc) enter with the organic matter play also a perceptible, although not decisive, role in organics removal.

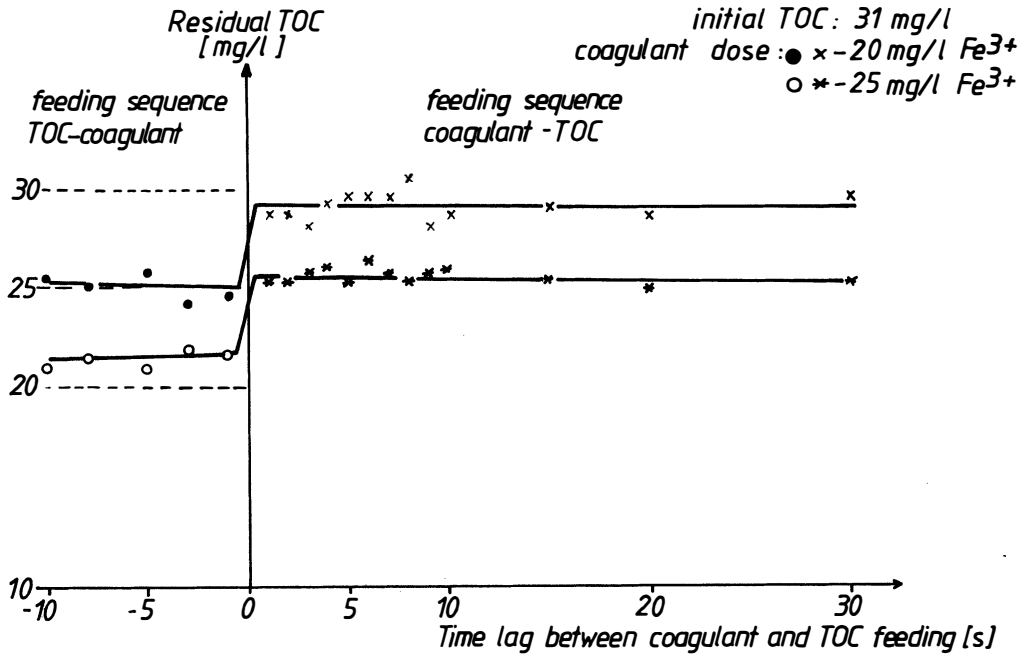


Fig.1. Residual TOC vs. the sequence of TOC and coagulant feeding

CONCLUSIONS

1. In the removal of the dissolved organic substances the aluminium or iron (III) hydroxide species which are still dissolved, but are transformed by polymerisation processes within a brief period of time (of a few seconds' order) into poorly water soluble metal hydroxides, are the most effective ones.
2. The durable bonds developing between the still dissolved aluminium hydroxide species and the organic substances are of the hydrogen-bridge type.
3. The negatively charged organic substances are adsorbed on the surface of the aluminium and iron(III) hydroxide sols which carry a negative charge, consequently the adsorption processes, along with the hydrogen bonds, contribute also perceptibly to the removal of organics during the coagulation-flocculation process.
4. In the light of experimental evidence, valence bonds between the various organic substances and the aluminium hydroxides in the course of coagulation-flocculation are unlikely to develop.