

# Natural Organic Matter in Drinking Water

## Origin, Characterization, and Removal

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## CONSIDERATIONS ON THE COLLISION EFFICIENCY FACTOR IN COAGULATION OF DISSOLVED NATURAL ORGANIC MATTER

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### 1. Introduction

Collision efficiency factor,  $\alpha$  (often referred also as sticking factor, sticking coefficient, collision agglomeration factor etc.) was developed and is used in mathematical description of both coagulation and sand filtration phenomena in water treatment as a correction for "non-ideal" behaviour of particles in real water systems. It is defined as a dimensionless ratio of the rate at which particles (molecules) actually aggregate to a rate at which particles collide. Not all collisions are successful in terms of producing an aggregate of the colliding particles. For an ideal and completely destabilized system  $\alpha = 1$ ; for a completely stable system, in which any collision does not produce an aggregate,  $\alpha = 0$ .

Much of the past research on coagulation was performed with waters containing inorganic suspended particles (turbidity). Experimental and theoretical research usually and quite understandably preferred the use of well defined particles. The jar test was, and still is, the most frequently used laboratory technique of testing the coagulation/flocculation response to the addition of coagulants into different types of waters.

Water resources, which are used for drinking water supply, usually contain very complex mixtures of substances and particles, which should be removed. Natural organic matter (NOM) is an important component of this mixture. But such major variations in features of pollutants may be an important source of discrepancies in at least two ways.

Firstly, molecules (e.g. of humic substances) and particles (inorganic, organic or microorganisms) in different waters may behave differently in comparison with the behaviour of suspensions containing inorganic particles only, which were studied in most theoretically oriented papers dealing with coagulation kinetics up to now.

Secondly, the classical jar test does not simulate well the processes which occur in different coagulation and separation technological units and in the different arrangements of technological processes used in real treatment plants. It was more or less tailored for the conventional treatment of turbid waters.

This second possible source of problems, which was mentioned above with respect to coagulation research, may be agreed or not. If it is at least partly accepted, it raises the question of whether or not the optimum chemical conditions for coagulation and separation should be assessed in a different way, and which way is the best.

It might be also discussed, what are the limits in interpretation of the jar test results in coagulation research and how many different tests would be necessary to create the whole picture? But such a question is rarely the case as it does not have enough push. In practice only a few treatment plants have made a detailed and fine comparison between jar test data and the plant separation performance under different operating conditions. If most of the plants are designed with some safety factor and operated at conditions resulting from the jar test, they usually "do well". Therefore operators do not have much motivation to do any research on how to perform a bit better if the standards are met.

As optimum dosing of chemicals is a topic of another upcoming workshop, it will not be further discussed here in detail. Let us focus on matters, which NOM may bring to theory and practice of coagulation in water treatment.

## 2. Considerations on collision efficiency factor in NOM coagulation

The progress in isolation, fractionation and characterization of NOM shows the interesting variety of chemical characteristics of substances we find in natural waters.

This is one of the key differences between turbid waters and waters containing NOM. Turbidity causing particles may be described relatively easily, usually by their size distribution, density and their surface characteristics. This is not the case in coagulation of NOM. We are only just beginning our search of the interactions between many possible NOM characteristics and their separability from water by different treatment processes.

The chemical characteristics of NOM are also the reasons for its difference in behaviour in comparison with the coagulation of inorganic particles. The best example is probably the one order of magnitude higher surface charge of humic substances as the same concentration of the of mineral particles. The second, and probably quite important difference between inorganic particles and NOM is that chemical reactivity of NOM (at least the humic part of NOM) changes with different molecular weight, i.e. different molecular

weight fractions generally react in a different way. Furthermore, the same molecular weight does not guarantee the same reactivity under different conditions, and more detailed further analysis of NOM fractions has to be considered. This is the starting point for the authors belief that some kind of black and white approach, which was quite successful and sufficient in the case of coagulation of inorganic particles, has to be refined in the case of NOM.

### 2.1. Does every NOM molecule have an individual value of the collision efficiency factor?

Collision efficiency factor, which was used as a part of a basic theoretical study e.g. by Hahn and Stumm [1], is apparently a mean value of the ratio of successful collisions between particles to all the collisions in the system. In the system studied in their work, consisting of one type of well defined mineral particles, this assumption is absolutely correct and precise and there is probably no need for further explanation.

To describe mathematically the floc growth process with the aim to use it for flocculator design, one may refer e.g. to Tambo's summarizing paper [2] where the author uses the term "initial collision agglomeration factor -  $\alpha_0$ ". This reflects the uncertainty that, even in the case of mineral particles which Tambo used for most of his experiments, the value of  $\alpha$  may change with the progressing aggregation in the system. There is not much information, either in [2] or elsewhere, not only about the calculation or measurement of changes of  $\alpha$  value during coagulation, but also about the scale and nature of such changes of  $\alpha$ .

Some quite remarkable preferences have already been reported in the removal efficiency of different fractions of NOM from waters, e.g. in [3-10]. What are the reasons for this phenomena? Better removability is preferentially attributed to such characteristics as higher apparent molecular weight or size, colour to DOC ratio, specific UV absorption, carboxylic group content etc.

Do all the collisions between molecules of different fractions follow the same probability of forming an aggregate, which is given by the value of the collision efficiency factor in the system?

The author hypothesizes that having isolated narrow fractions of NOM, each of them would have a different value of  $\alpha$  (of course in a chemically identical "rest" of the water system). Such a value may be an important characteristic of each fraction from the coagulation point of view. In such case we can write,

$$Q_{NOM1} = Q_{NOM2} = Q_{NOM3}$$

(1)

where:  $NOM_1, NOM_2, \dots, NOM_n$  are fractions of the bulk mixture of NOM.

The second step hypothesis could be:

Every fraction of NOM has the highest  $\alpha$  value at different chemical conditions in the water system.

These chemical conditions are usually represented by pH and dose and type of coagulant, but some other variables may also be considered (e.g. ionic strength, type of hydrolytic products of coagulant). This is illustrated in Figure 1, where hypothetical change of any system chemistry variable is denoted as "System variable  $x_1$ ". Changes of values of different variables (i.e. also their different combinations) produce a multidimensional field of influences on "individual  $\alpha$  values" of different fractions.

Similarly to the previous approach, Bache and Hossain [11] studied responses of floc characteristics in the two dimensional field of pH and Al dose. They found that zones of maxima of important floc parameters (settling velocity, strength of flocs, floc size, effective density, residual Al and colour), are not the same, and tendencies of their maxima differ substantially. It was not easy to find explanations for some of their results and some remained unexplained. Some similar peculiarities resulting from multidimensional studies of coagulation of humic waters which, besides chemical variables, also included temperature, were also reported in [12, 13] and they seem to be in agreement with [11].

## 2.2. Possible consequences of concept of "individual $\alpha$ " for water treatment practice.

As an example, let us define  $\alpha_{1,1}=0.2$  and  $\alpha_{2,2}=0.02$  for collisions between molecules of two different fractions of NOM under the same chemical conditions. If both molecules have about the same characteristic dimensions and concentration, the first one will aggregate ten times faster than the second one.

If we return to Figure 1, it is clear that under the same concentrations and molecular size of all three NOM fractions, the system will be dominated by the high  $\alpha$  of the  $NOM_1$  fraction and  $x=3$  will be probably determined as optimum for coagulation in the whole system.  $NOM_2$  and  $NOM_3$  will be considered as only hardly removable because of their low value of  $\alpha$  at  $x=3$ . This "non removability" of  $NOM_2$  and  $NOM_3$  will be evaluated as even worse if their molecules are smaller than  $NOM_1$ .

On the other hand individual  $\alpha$  of different fractions

may change with change of chemical conditions. It was already published that "different chemicals and different treatment conditions with the same chemical can bring about destabilization of fulvic acids by different mechanisms" [6]. There may be a combination of conditions under which fractions  $NOM_2$  and  $NOM_3$  will possess higher  $\alpha$  than under hypothetical conditions in Figure 1. Then, it has to be answered, under which conditions is a plant operation technologically feasible including decision on sequential dual (or multiple) operation at different conditions.

Such technological option is probably already successfully introduced into practice in many places. The example is coagulation with different coagulants and/or at two different pH's. The author has his own very positive practical experience with such treatment arrangements.

There is another technological design pattern, which could be reevaluated in future - residence time in coagulation/flocculation tanks and a design tendency to produce large settleable flocs and remove them from the system as soon as possible. This probably does not allow parts of NOM having low  $\alpha$  values to aggregate into separable particles. If large particles (i.e. those formed from NOM fractions with high  $\alpha$ ) would stay in suspension, they may serve as aggregation centers for other NOM molecules which may be either smaller or which may have lower individual  $\alpha$  or both. There may be many installations where even such extensive factors like long residence time in "aggregation reactors" would still be an economical option if e.g. oxidation or adsorption units could be abandoned by this way. Some experimental support for this suggested option may be found in [14, 15].

A new question to be answered in future is, which hydrolytic products of coagulants are the most effective in destabilizing different fractions of NOM? We have to consider that some of them have a very short life-time. Recent results of Klute and Hahn [16,17] brought something like a new dimension further into coagulation research - homogenization of coagulant with raw water. Homogenization practiced in most jar test studies was usually less effective than the fastest technically possible (i.e. within a few tenths of a second), which seems to be much needed.

## 2.3. Future expected complications

Up to now,  $\alpha$  was usually defined for collisions between molecules or particles as if they were both destabilized to the same extent. If there is an "individual" value of  $\alpha$ , which is characteristic for collisions between molecules which belong to the same narrow fraction of NOM, we have to think of the  $\alpha$  value

which is effective for collisions between NOM molecules, which belong to different fractions.

The question to be solved is, what value of  $\alpha$  shall we expect for collisions between the molecules, which belong to different fractions? Will collisions between the different molecules follow the laws of probability calculations or shall we expect some "inconsistency"?

### 3. Summary

Collision efficiency factor  $\alpha$  between NOM molecules, which belong to the same fraction of NOM, could differ from  $\alpha$  between molecules, which belong to another fractions of NOM.

Every fraction of NOM has the highest  $\alpha$  value at different chemical conditions in the water system. Coagulation at different conditions could enhance destabilization and aggregation of higher total amount of NOM.

Progress in both NOM research and treatment practice could be made by understanding the specificity of reactions of various fractions of NOM with coagulants. Next research step could be study and verification of individual behaviour of fractions in mixture with other fractions. This will help us understand the role of NOM from the coagulation point of view.

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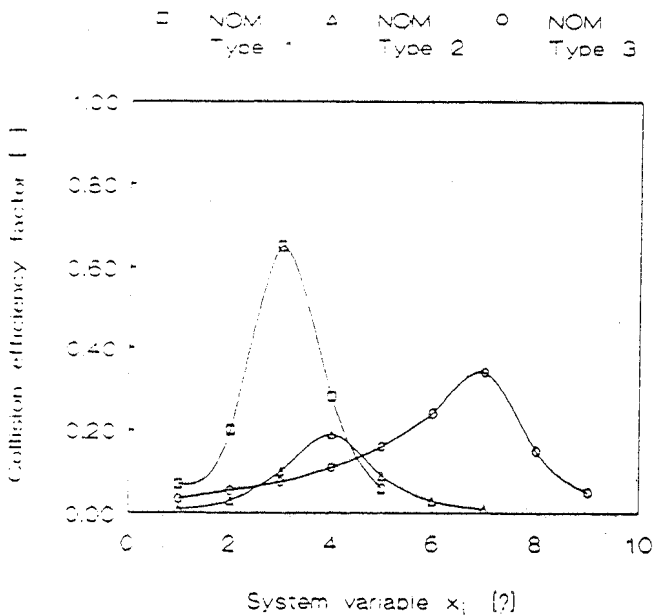


Figure 1.

Hypothesized influence of a system variable  $x_1$  on the collision efficiency factor  $\alpha$  between the same molecules of three different fractions of NOM.