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## Atom-to-Enterprise: Multi-scale Modeling of Flocculation Processes

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### Abstract

The flocculation process is an important step towards product purification in downstream bio-manufacturing, and for removal of organics, biomass and cell debris in wastewater treatment. Despite a broad application in various industries, the process mechanism is not well understood. Flocculation is a process that can be represented across scales, from nano-scale and all the way beyond the microscale. Due to the current lack of knowledge for modeling flocculation across the length scales, industry often resorts to manual control or no control at all of flocculation processes. In this work, it is intended to develop a hybrid systematic model-based framework, which integrates computational chemistry and stochastic modeling approaches for monitoring and control of the flocculation process above micro-scale. The intention is to reduce the time required for manual control, and to avoid potential product losses in addition to unwanted process variations during operation.

**Keywords:** Flocculation, Process Modeling, Computational Chemistry, Artificial Intelligence

### Introduction

Flocculation has several applications in the food industry, for clarification in water and wastewater treatment, and in bio-based production in conjunction with microfiltration to pretreat the biological feeds before filtration, since they are highly non-Newtonian and the cake formed is highly fouling. One way of improving the filterability is to treat them before microfiltration by flocculation process [1]. For such a flocculation process, in order to develop an appropriate model-based understanding of the kinetics governing the system, it is necessary to study the stability of emulsion systems [2]. Given the immense application of this process across the industry, many studies have put efforts in developing kinetic models describing emulsion stability in flocculation [3].

Flocculation, as illustrated in Figure 1, is a process in which two or more particles of the dispersed phase collide and cluster as an aggregate. The process includes aggregation, fragmentation, breakage and erosion phenomena. In this study, a basic mathematical model is used to determine the particle size distribution over the time of the process operation. The first and third terms in Eq. 1 account for the generation of flocs of size class  $i$  due to aggregation of smaller size aggregates and fragmentation of larger size aggregates respectively, while the

second term represents the destruction of such aggregates due to fragmentation, and the remaining terms stand for the destruction of flocs considering breakage and erosion [4].

$$\frac{dN_i}{dt} = \sum_{\substack{j \geq k \\ v_{i-1} \leq (v_j + v_k) \leq v_{i+1}}} (1 - \frac{1}{2} \delta_{j,k}) \eta_i \alpha_{j,k} \beta_{j,k} N_j N_k - N_i \sum_k \alpha_{i,k} \beta_{i,k} N_k + \sum_k \gamma_{j,i} S_j N_j - S_i N_i \quad (1)$$

Where  $N_i$  is the number of flocs in size class  $i$ ,  $v_i$  stands for the volume of a size class  $i$ .  $\delta_{j,k}$  is the delta-dirac function in order to avoid considering the collisions twice,  $\eta$  is a proportional coefficient that shows how the generated floc size should be assigned to the size classes of the model, while  $\alpha$  is the collision efficiency and  $\beta$  is the kernel corresponding to aggregation.  $S$  is the breakage kernel and  $\gamma$  is the breakage distribution function that determines the fraction of daughter particles in each size class. The population balance model is then implemented with the python based package TensorFlow in a hybrid framework [5].

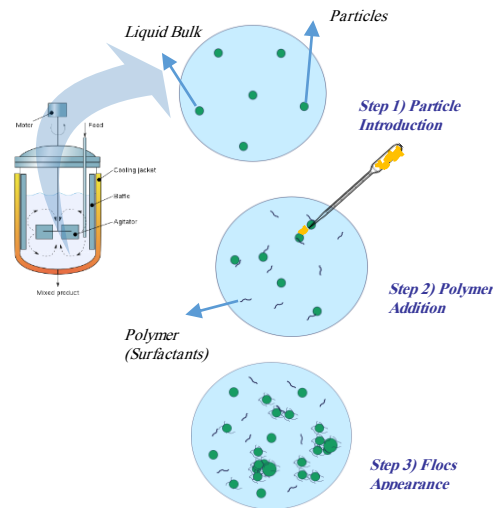


Figure 1: Schematic figure of a flocculation process in three sequential steps

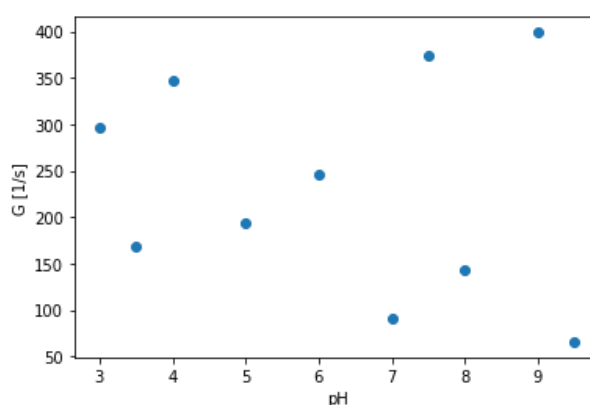
In this work the intention is to develop a hybrid model-based framework that combines computational chemistry with data-driven methods to train the model. The framework integrates computational chemistry as the means to quantify the surface interactions between the particles in the system. As such, density functional theory (DFT) is being employed to conduct a geometry optimization on the polymer with Turbomole®. Then possible conformers are calculated by using COSMOconfX® with BP-TZVPD-FINE basis set. These conformers are then introduced to COSMOthermX® with silica particles to generate the sigma surfaces for both molecules. These sigma surfaces are necessary for the calculation of interfacial tension between the particles. In order to calculate the interfacial tension for this system, a model of such property for the solid-liquid interface is being employed based on the liquid-liquid interfacial tension in Andersson et al. [6].



The machine learning model consists of a deep learning algorithm and is utilized to find the kinetic law governing flocculation using image analysis at microscale. The framework is structured such that the data collected from the first-principles model is utilized to determine the parameters required for the kinetics of this process. The machine learning algorithm consists of different hidden layers to train the deep learning algorithm. An experimental setup is prepared for collection of data for the model. Thereby, the machine learning algorithm receives both molecular simulation data and measurements from the experimental setup. The in-line measurements can provide various floc properties for the deep learning algorithm. The best fitting kinetic expression governing the system can then be found by the integration of the first principles model, machine learning algorithm and the data collected from the experiments. Subsequently, the particle size distribution is predicted by the PBM model and the results are compared with the experimental results to validate the model.

### **Experimental**

In order to carry out the experiments for silica particles flocculation, a literature study has been carried out to determine the most important parameters for such system. Among different variables influencing the process, pH and shear induced in the system by a stirrer are studied in this work. Hence, a design of experiments (DoE) is conducted using the Sobol method [7]. The Sobol method applies a quasi-random sequences over the parameter space. This will allow to re-use the measurements when conducting more physical experiments with additional process parameters and to use the same sample set for the computational model by applying Monte Carlo based statistical analysis. In this way a cyber-physical setup for the automation of experiments in future research work will be prepared. The range of pH values that is tested is 2-10 and the velocity gradient induced by the stirrer is defined in the range of 50-500  $s^{-1}$ . The search space for carrying out the experiments is illustrated for 10 sampling points in Figure 2.

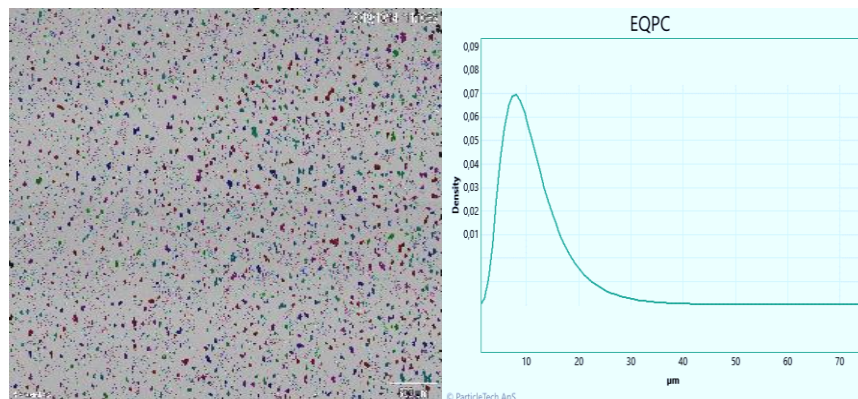


**Figure 2: Sampling points proposed by the Sobol method for DoE**

Currently, an initial experiment is conducted with borosilicate particles in demineralized water to see if the image analysis device (oCelloscope by ParticleTech ApS) can perform a fine segmentation on these particles. As such, a very simple setup is provided with a solution of borosilicate in demineralized water. A very small sample of the suspension is placed in a well plate. The plate is then placed in the oCelloscope to perform the image analysis. The



particle size distribution of the particles after 10 min in water solution is represented in Figure 3. The colorful objects in the image shows that the borosilicate particles can be perfectly identified by the image analysis algorithm.



**Figure 3: Image segmentation of borosilicate in distilled water after 10 min and corresponding size distribution**

It is intended to carry out the core experiments with the discussed DoE and a new experimental setup. The experimental setup illustrated in Figure 4 consists of the oCelloscope and a peristaltic pumping system that pumps a sample with a specific flowrate through the flow-cell in oCelloscope. The pump is located after the flow-cell to avoid any influence on the particles before taking the images. A reactor setup (developed by Applikon Biotechnology) is also used to provide the pH and impeller velocity control system. The primary sample of silica particles is from Sigma Aldrich with CAS number: 7631-86-9. The initial size distribution of the particles is in the range of 0.5-10  $\mu\text{m}$ . A silica suspension of 0.02% wt is prepared in demineralized water in a glass type reactor of 100 ml. A pH probe is provided in the reactor to measure the pH during the experiments. The reactor has an impeller that provides the shear for flocculation. An on-line image analysis is being carried out by pumping 40  $\text{ml}/\text{min}$ . It is intended to determine the particle size distribution every 5 min for half an hour during the process to have a better understanding of the process variations with respect to time for the pH range of 2-10. During the experiments the velocity gradient is constant and equal to 290 rpm.

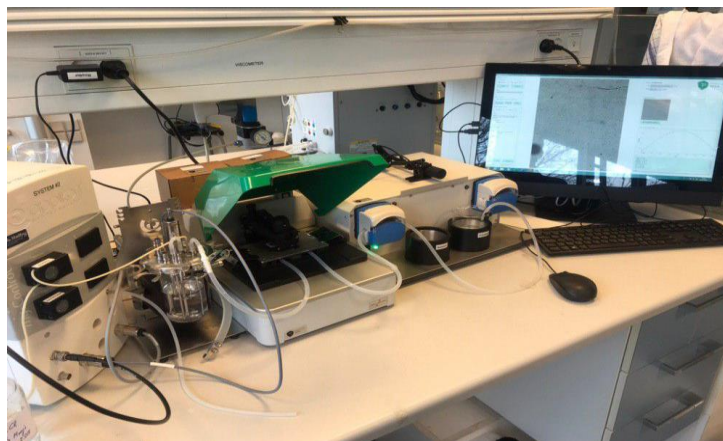


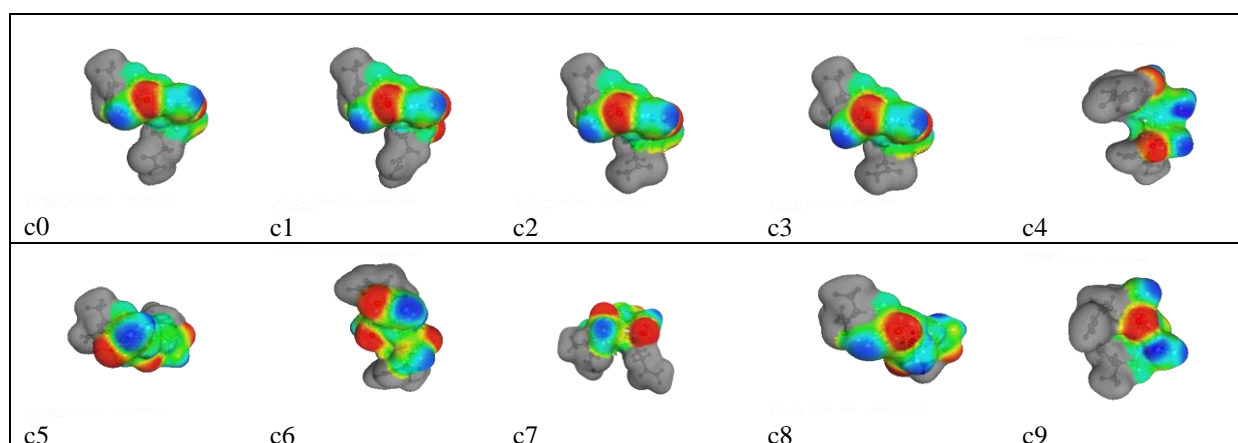
Figure 4: Experimental setup

### Results and discussion

In order to determine the interactions between a surface (i.e., polyacrylamide) and polymer-coated particles (e.g. silica nanoparticles) in the system we use molecular simulation. The sigma surfaces for 10 possible conformers of the polyacrylamide molecule is determined by COSMOconfX®. In order to build the polyacrylamide molecule, a pentamer of such molecule is first built in Avogadro® and the geometry optimization is carried out by using Turbomole®. Different conformers of such a pentamer are then determined by using COSMOconfX®. The conformers of this molecule is then used in COSMOthermX.

For all of the conformers, it is considered that the weight fraction of the two edges of the molecule is zero. It is an approximation of a larger polymer chain, where the edge effects will be minimal and the ends of the model molecule will not be included. As such a pentamer of polyacrylamide has been chosen for the simulation of the polymer in order to avoid a too large effect of the edges in further calculations. All determined conformers are illustrated in Table 1.

Table 1: Sigma surfaces of polyacrylamide conformers







### **Conclusions**

In this work it is shown that silica particles suspension in water can be perfectly observed with the oCelloscope and corresponding image analysis algorithms. A fine segmentation is performed on this system. Hence, most of the silica particles in the sample can be identified by the segmentation algorithm and the process of silica flocculation can be monitored by the experimental setup above microscale. In order to have a phenomenological understanding of the process in nano-scale (i.e. non-observable state) a DFT calculation is carried out to determine all possible conformers of polyacrylamide molecule, because this polymer is one of the polymers mostly employed for silica particles flocculation. It can clearly be seen from the conformers presented in Table 1 that each conformer has different sigma surfaces. Therefore, the interactions between polymers, silica particles and the solution will depend on the conformation of the polymer, and therefore all conformers are included in the calculation to be able to model the molecular properties under a range of conditions. In the next step of this study it is intended to determine the sigma surface for silica particles and calculate the solid-liquid interfacial tension between silica and polyacrylamide molecule. Moreover, the population balance model of flocculation is under implementation in the aforementioned TensorFlow model to combine it with machine learning algorithm.

### **Acknowledgements**

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