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ABSTRACT

Over the years, because of fast growth of population and industrial activities, we have increasingly polluted ou waters. Conventional water treatment processes become indequate with the identification of new contaminants in the water. To overcome these challenges, a particular emphasis is accorded to the implementation of environmentally, eco-friendly and less-energy technologies for water treatment processes. In this context, we investigate wether new chemical treatments employing organic polymers are efficient enough to provide green solutions for waste water recycling. We focus our attention on stabilized colloidal suspensions that show no sedimentation rate. In order to destabilize these colloids, two mechanisms are mainly involved: coagulation and floculation. These mechanisms depend on the aggregation rate between particles modelised by the Smoluchowski's coagulation equation. In this paper, we study the number concentration of coagulated particles and we show more the time step decreases, more the error on moments of order 0 decreases for a certain number of particles.

Keywords: *Pollution, Polymers, Colloids, Simulation, Smoluchowski equations, Monte Carlo method*

GLOSSARY

Symbols :

c number of polymers
K coagulation kernel
$\check{c}$ mass density
$M_{0,N}$ approximate moment of order
M_0 exact moment of order

Index :

i,j polymer length
N number of particles
t time
Δt time step

1. INTRODUCTION

In order to provide a sustainable development and to avoid the negative impacts on our environment, green chesmistry science and technology offers economically alternatives for chemical water treatments by taking into account the protection of public health and the environment. These techniques are carried out by adding organic polymers which may replace the inorganic coagulants in order to meet the green treatment goals.

The conventional methods of solid-liquid separation such as filtration, sedimentation, centrifugation and flotation, for urban waste process water treatment cannot be used directly on stabilized colloids suspensions that show no sedimentation rate despite the existence of density variation between the two phases. For waste water treatment, difficulties occur when the particle size allows it to remain in suspension in the liquid medium. Classical decanting mechanism is possible when the pretreated water stays in calm waters in the primary settling basin where suspended materials are deposited in the bottom to be scraped and evacuated. But it is unfortunately not enough because the time of decantation of a colloid takes between 2 and 200 years. Colloids are particles of sizes varying between 10^{-2} and 1 μm and are generally negatively charged. Actually, colloids have a surface activity which has an appreciable influence on the properties of the aggregate. This phenomena governs the stability of colloidal suspensions which results from the balance between the attractive energies of Van der Waals, which favor aggregation, and the electrostatic repulsion energies. The decantation is carried out by adding polymers whose function is to agglomerate the solid particles in the form of flocs and thus to increase the rate of sedimentation. There are two ways of producing changes in the state of agglomeration of suspensional colloids defined by the terms coagulation and floculation.

In fact, the colloid moves in the the solution with part of its electric double-layer repulsion. The first layer is fixed to the colloid surface and the second is more diffuse. The potential difference between the first layer and the solution is called the zeta potential which governs the displacement of the colloids and their mutual interaction [1, 2]. To destabilize the suspension and promote the agglomeration of the colloids, it is necessary to cross the energy barrier and thus to reduce the zeta potential so that the Van der Waals forces as well as the surface adsorption phenomena become dominant again. This kind of aggregation is known as coagulation. This destabilization is achieved by coagulation polymers of Low Molecular Weight with a high cationic charge in order to neutralize the negative charges of the colloids. Having become true dipoles, these particles are attracted to each other and collide with each other due to the momentum of Brownian motion.

After colloidal suspensions have been destabilized, flocculants polymers are frequently used because of their very High Molecular Weight, i.e. high degree of monomer polymerization. These flocculants are extremely effective in bonding the micro-flocs formed during coagulation by using long polymer chains. The polymer chain in solution is partially adsorbed on a particle beyond its double layer and when other particles are close enough, the elongate chain is adsorbed on its surface and creates bridging between the two particles. In general, the efficiency of the polymer depends on the molecular chain lengh, because more the chain is longer more the probability of creating bridging is greater.

2. MATHEMATICAL MODEL

For a given polymer, bridging mainly depends on two parameters: the number of sites available for adsorption on the colloids surface and the rate of polymers agglomeration. One can consider that the probability of two polymer chains fusion is proportional to their lengths sum.

The beginning of the classical understanding of colloidal aggregation stem from the work of Smoluchowski on coagulation processes in colloids [3], a population equilibrium equation which describes in statistical chemical physics the agglomeration which follows from the assumption that the collisions are binary and that fluctuations in density are sufficiently small so that the collisions occur at random. The Smoluchowski equation is of universal use in the fields of colloid chemistry, aerosol dynamics and Nanotechnology Science. It is to say that the collision rate per unit length is due to the Brownian motion and the particle agglomeration rate depends on

the particles contact probability and the effectiveness of the latter. Numerical resolution of the Smoluchowski equation is obtained employing the Monte Carlo technique [4] and its alternatives methods.

If the polymers are assimilated to their chain length and if we consider that two polymers of respective lengths i and j have a probability *K(i,j)* to coagulate to give a particle of length *i+j*, a balance of continuous equation makes it possible to obtain the integro-differential equation [5]:

$$\frac{\partial c}{\partial t}(i,t) \;=\; \frac{1}{2}\sum_{j=1}^{i-1} K(i-j,j)\,c(i-j,t)\,c(j,t) \;-\; \sum_{j=1}^{\infty} K(i,j)\,c(i,t)\,c(j,t)\,, \qquad \forall i \in \aleph^*, t>0,$$

$$K(i,j) \;=\; i+j \quad \text{and} \quad c(i,0) \;=\; c_i(0) \;=\begin{cases} 1 & if\ i=1, \\ 0 & else. \end{cases}$$

where *c(i,t)* denotes the number of polymers of length *i* at time *t* and *K(i,j)* the coagulation kernel. Physically, we assume that the number and total length of the polymers are finite and that *K(i,j)* is nonnegative and symmetric. The first term on the right-hand side represents the rate of agglomeration of polymers of length *k* by agglomeration of any polymers pair of length *i* and *j*, such that *i+j =k*. The second term accounts for the loss of polymers of length *k* by agglomeration with any other polymers chains.

Rather than approximating the density, we shall approximate the mass density which satisfises the following equation:

$$\frac{\partial \check{c}}{\partial t}(i,t) \;=\; \frac{1}{2}\sum_{j=1}^{i-1} \check{K}(i-j,j)\,\check{c}(i-j,t)\,\check{c}(j,t) \;-\; \sum_{j=1}^{\infty} \check{K}(i,j)\,\check{c}(i,t)\,\check{c}(j,t), \qquad \forall i \in \aleph^*, t>0\,,$$

$$\check{c}(i,0) \;=\; \check{c}_i(0), \quad \text{where} \quad \check{c}(i,t) \;= i\,c(i,t) \quad \text{and} \quad \check{K}(i,j) \;=\; \frac{K(i,j)}{j}.$$

An analytical solution of the problem is given by:

$$c(i,t) = e^{-t}\;\frac{i^{i-1}}{i!}\;(1-e^{-t}\;)^{i-1}\;e^{-i(1-e^{-t}\;)}\,, \quad i \in \aleph^*, t>0.$$

We compute the solution up to time T=2 for different time steps varying from $\Delta t = \frac{T}{100}$ to $\Delta t = \frac{T}{1000}$ and for several particle numbers varying from N=10^4 to N=10^5 and we compare the approximate moment of order 0 which corresponds to the number concentration of coagulated particles which decreases with the growth of the particle size:

$$M_{0,N}(t) = \sum_{k=1}^{N} \frac{1}{i_{N,n}(k)}$$

to the exact moment of order 0 over the interval [0, 2]:

$$M_p(t) = \sum_{i=1}^{\infty} i^p\,c(i,t) = \sum_{i=1}^{\infty} i^{p-1}\;\check{c}(i,t) \quad where \quad M_0(t) = \;e^{-t}\;.$$

3. SIMULATION RESULTS

There has recently been a great deal of interest in the computer simulation of aggregation phenomena in order to confirm the theoratical studies. In [6], we have studied the moments of order 0 and 2 and we have shown that the method sems to be more accurate approximating numerically the first moment than the second one usually used as an index to characterize the total light scattered, which increases with the growth of particle size and polydisperity. In this paper, we focus our study on the moment of order 0 and we show that the time step Δt influence the error on moment in such a manner that the error varies between 10^{-2} and 10^{-4} for Δt varying between $\frac{1}{100}$ and $\frac{1}{300}$. Most of the results reported in this paper were obtained from simulations in which the effective total number of colloidal suspensions was varying between 10^4 and 10^5.

Simulations were performed for a time step Δt varying between $\frac{1}{100}$ and $\frac{1}{300}$ and five effective total number of particles. The following table shows that considering a certain number of particles *N*, more the time step Δt decreases, more the error on moments of order 0 $\boldsymbol{M_{0,N}}$ decreases. These results prove the precision of the method employed in this paper.

Error on $M_{0,N}$	***N*=3x10⁴**	***N*=5x10⁴**	***N*=7x10⁴**	***N*=8x10⁴**	***N*=10⁵**
$\Delta t = \frac{1}{100}$	0,013736	0,004121	0,002829	0,003407	0.003148
$\Delta t = \frac{1}{200}$	0,002576	0,002876	0,000602	0,002224	0.001073
$\Delta t = \frac{1}{300}$	0,000612	0,000632	0,000356	0.000890	0.000073

Table 1: Variation of the error on moment of order 0 in fonction of the number of particles and the time step.

The following simulations show the validity of the Smoluchowski theory approach with comparing results of computer simulations.

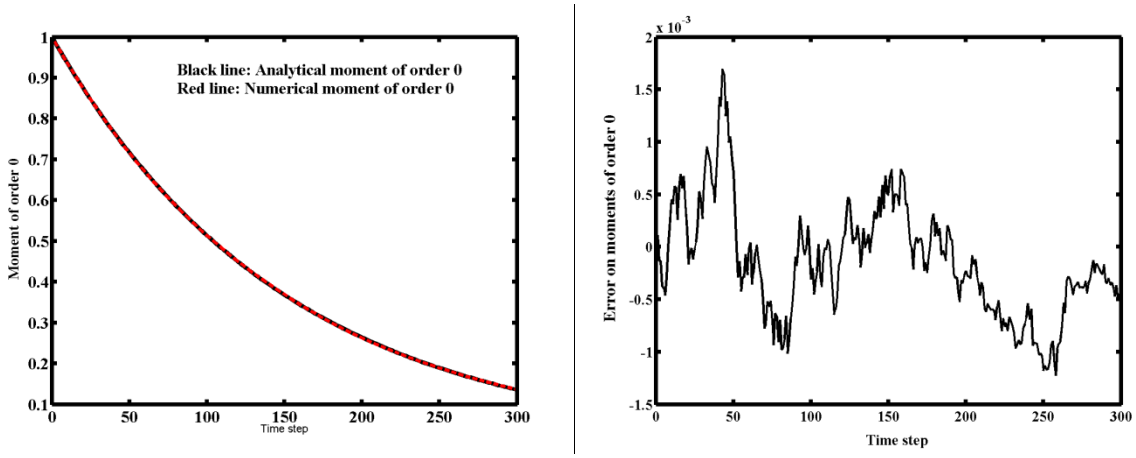

Figure 1: Comparison between analytical and numerical moments of order 0 (left) and the error on moments of order 0 (right) corresponding to *N*=7x10⁴ for $\Delta t = \frac{T}{300}$.

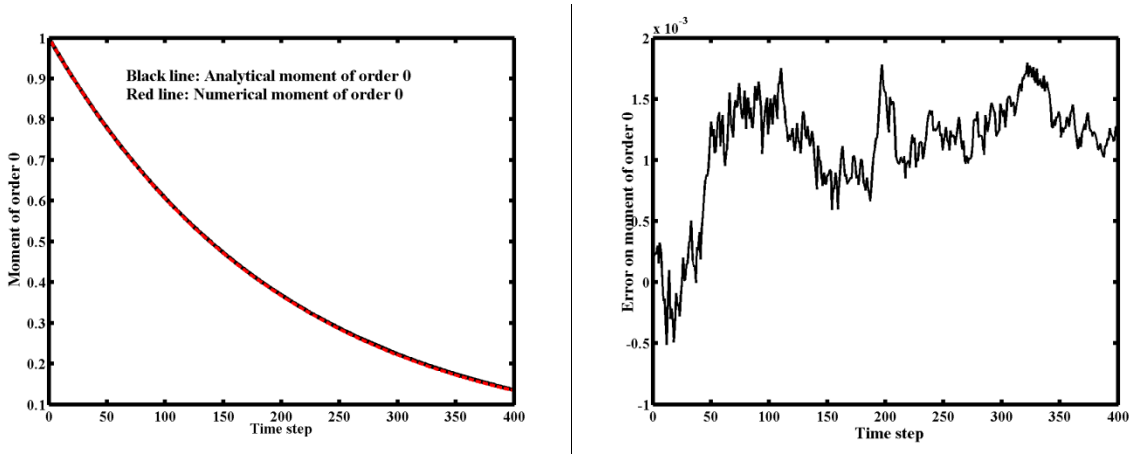

Figure 2: Comparison between analytical and numerical moments of order 0 (left) and the error on moments of order 0 (right) corresponding to N=8x10^4 for $\Delta t = \frac{T}{400}$.

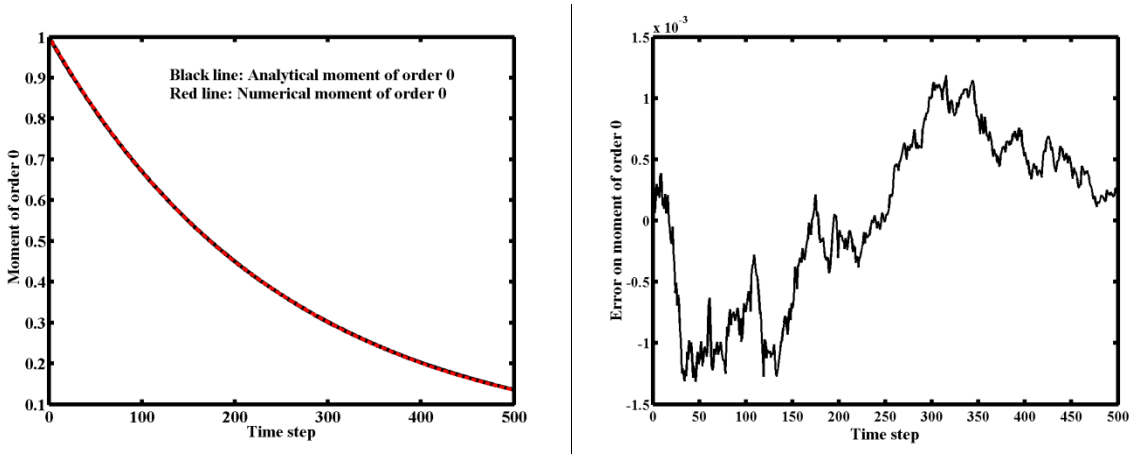

Figure 3: Comparison between analytical and numerical moments of order 0 (left) and the error on moments of order 0 (right) corresponding to N=10^5 for $\Delta t = \frac{T}{500}$.

Other simulations were carried out for various time steps varying between $\Delta t = \frac{1}{10}$ and $\Delta t = \frac{1}{60}$ corresponding to a number of particles of order 10^4, in order to show the influence of the time step on the error on moment of order 0. One can see that more the time step decreases, more the error decreases solution and the method is validated.

Δt	**Error on $M_{0,N}$**	Δt	**Error on $M_{0,N}$**
$\Delta t = \frac{1}{10}$	-0.0028516	$\Delta t = \frac{1}{40}$	0.0058930
$\Delta t = \frac{1}{20}$	0.0073008	$\Delta t = \frac{1}{50}$	0.0046693
$\Delta t = \frac{1}{30}$	0.0061412	$\Delta t = \frac{1}{60}$	-0.0005551

Table 2: Variation of the error on moment of order 0 corresponding to N=10^4 in fonction of the time step.

4. CONCLUSIONS

In this paper, we have analysed an approach for solving Smoluchowski's coagulation equation using the Monte Carlo method in order to simulate the aggregation of polymers employed in the waste water process treatment. Our study provides numerical evidence that the numerical method seems to be accurate approximating the zeroth moment representing the particle number concentration, which decreases with the growth of the particle size. We have shown that the time step influence the error on moment in such a manner that considering a certain number of particles, more the time step decreases, more the error on moments of order 0 decreases.

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