

## Modeling of controlled particle deposition onto electronically conducting surfaces

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### Abstract

Deposition of colloidal particles onto surfaces is usually assumed to follow the Derjaguin-Landau-Verwey-Overbeek (D.L.V.O.) theory for colloidal stability. In the work presented here the D.L.V.O theory is extended to include the case where the surface is electronically conducting. The effect of application of an electric field to the surfaces on the rate of deposition of 5.4  $\mu\text{m}$  colloidal particles is simulated.

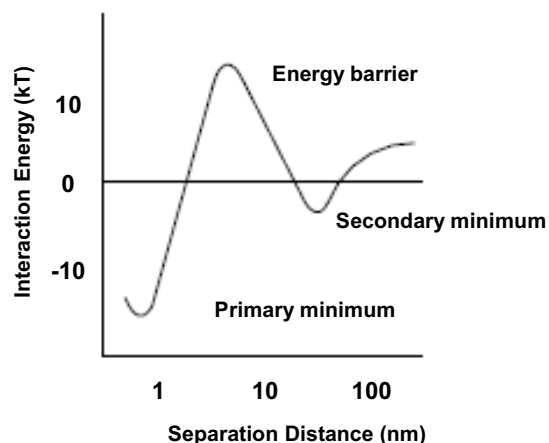
**Keywords:** DLVO, colloid, deposition, Trajectory Analysis

### Theoretical Background

Deposition of colloidal particles occurs in two steps; (1) the transport step whereby particles are brought to the vicinity of the collector by fluid flow and diffusion (2) the attachment step whereby particles are deposited on the surface by means of electrostatic forces. The Derjaguin-Verwey-Landau-Overbeek (D.L.V.O.) theory assumes that the forces operating between colloidal particles in suspension comprise the electrostatic double layer and the attractive van der Waals, and the sum of these two forces constitute the total force keeping colloidal particles in suspension.

Predictions based on the D.L.V.O. theory suggest the occurrence of both favourable and unfavourable deposition conditions when overall attractive and repulsive energies exist between surfaces, respectively. Indeed many experimental results in the literature confirm

the occurrence of favourable and unfavourable deposition conditions [1-5].



**Figure 1.** Variation of interaction energy with distance for two surfaces

In a previous study, Bahmani [6] carried out

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deposition experiments of 5.4  $\mu\text{m}$  polystyrene latex particles onto Reticulated Vitreous Carbon (RVC) acting as the working electrode in an electrochemical adsorption cell shown schematically in Figure 2. The main objective of the experiments was controlling the rate of deposition by controlling the RVC collector potential by means of applying external electrical potential. The experimental results indicated that at a low electrolyte flowrate of 1.7  $\text{cm}^3/\text{min}$  the contribution of hydrodynamics to the deposition process was negligible compared to the surface forces. It was also concluded that at this low flowrate, it was possible to control the rate of deposition of colloidal particles by means of an applied electric field to the RVC electrode.

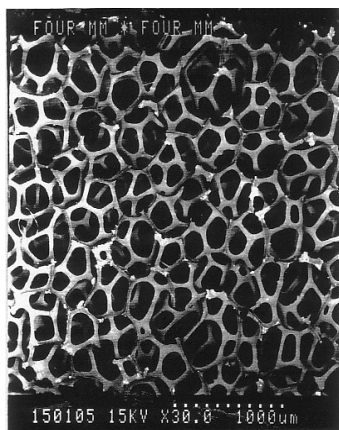


Figure 2. S.E.M photograph of Reticulated Vitreous Carbon (RVC)

Figure 2 shows the SEM of the RVC collector used in these experiments. As can be seen, the RVC is a rigid foam-like structure consisting of hexagonal units. One of the assumptions for the use of the trajectory analysis in this work is that the collector elements act as cylinders of 37  $\mu\text{m}$  length in so far as the effect of hydrodynamics is concerned.

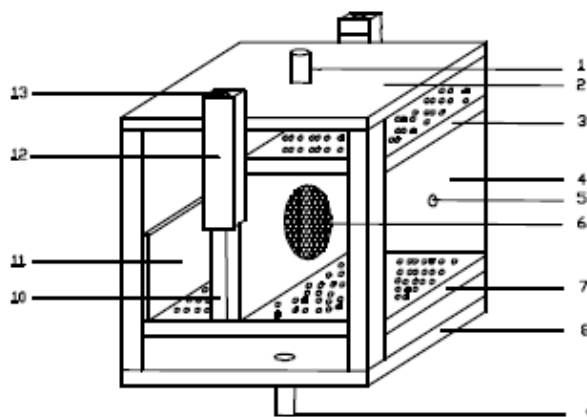


Figure 3. Schematic representation of the electrochemical adsorption cell 1): inlet, 2): top perspex cover, 3): perforated upper distributor, 4): area for RVC slab, 5): hole for wire connecting RVC slab to potentiostat, 6): membrane, 7): bottom perforated plate, 8): bottom perspex cover, 9): outlet pipe, 10): perspex membrane carrier, 11): stainless steel counter electrode, 12): 'side arm' for reference electrode, 13): hole for insertion of reference electrode

Figure 3 shows the schematic of the electrochemical adsorption cell used in these experiments. A rectangular slab of RVC was cut and placed in the cell, and then connected via a wire to a potentiostat. The RVC acted as the working electrode in the cell. A stainless steel plate was placed opposite to the RVC and acted as the counter electrode. A Standard Calomel Electrode (SCE) was used as the reference electrode [6].

Deposition of colloidal particles can be analysed by the convective-diffusion equation. However, convective diffusion equation involves solving the boundary value partial differential equation, and the later techniques are usually expensive in computational time. Recently attempts have been made to use techniques such as the Monte Carlo, Brownian dynamics, molecular dynamics and dissipative particle dynamics [7-10]).

Trajectory analysis was first used by Yao et al. [11], and since then this technique has been extensively used [8,9,10]. Trajectory analysis is, in fact, a force balance on a particle approaching the collector and is best

suiting for non-Brownian particles with diameters greater than 1  $\mu\text{m}$ .

In this work a modification of the formulation used by Spielman et al. [15] will be used to simulate experimental results. The starting point in this model is to specify the force due to hydrodynamics as the particle approaches the collector.

In essence the hydrodynamical interaction between the particle and the collector is estimated as follows. At a small particle distance from the collector the fluid flow around the collector is assumed to be undisturbed by the presence of the particle. At close distances, correction factors due to the presence of the particles are imposed on the undisturbed flow around cylindrical collectors.

The Navier Stokes and continuity equations describe the hydrodynamics of a fluid:

$$\begin{aligned} \frac{\delta U}{\delta t} + U \cdot \nabla U + \frac{1}{\rho_f} \nabla P &= \nu \nabla^2 U \\ \nabla U &= 0 \end{aligned} \quad (1)$$

Neglecting inertia and for incompressible fluids, the creeping flow equation results:

$$\begin{aligned} \nabla P &= \mu \nabla^2 U \\ \nabla U &= 0 \end{aligned} \quad (2)$$

Assuming that the no slip condition applies at the collector and particle surfaces, and also at a distance of a few particle diameters from the collector the fluid follows the undisturbed motion around a cylinder. Spielman [15] obtained the following relationship for fluid motion around a cylinder:

$$\varphi = 2 A_f U a_f^{-1} (r - a_f)^2 \sin \alpha \quad (3)$$

In which the constant  $A_f$  was given as:

$$A_f = 0.5 \left[ 1 - \ln \left( \frac{2\rho_f a_f U}{\mu} \right) \right]^{-1} \quad (4)$$

Colloidal particles are much smaller than the collectors and at a short particle distance from the collector surface the fluid is undisturbed by the presence of the particle. At close distances of separation, the collector is assumed to act as a plane and the velocity of colloidal particles is resolved into two components: a radial,  $V_R$ , and a tangential,  $V_\alpha$ .

Assuming that Stoke's law applies, the radial velocity is given as:

$$v_R = \frac{dh}{dt} = \frac{F_n F_1(H)}{6\pi \mu a} \quad (5)$$

In which  $F_1(H)$  is the hydrodynamics correction factor accounting for the influence of the presence of particles on the undisturbed flow past a cylinder and Spielman [16] has provided the following relationship for its estimation:

$$\begin{aligned} F_1(H) &= h & \text{for } h < a < a_f \\ F_1(H) &= \left[ 1 - \frac{9}{8}(H+1)^{-1} \right] & \text{for } a < h < a_f \end{aligned} \quad (6)$$

$F_n$  gives rise to the radial velocity of the particle consisting of hydrodynamic and external forces:

$$F_n = F_{st} + F_{ext} \quad (7)$$

Upon dimensional analysis the following relationship for the hydrodynamics component is obtained:

$$F_{st} = -6\pi \mu a^3 a_f^{-2} A_f U \cos \alpha_p F_2(H) \quad (8)$$

$F_2(H)$  is the hydrodynamics correction factor estimated using the relationship provided by Spielman [16]:

$$F_2(H) = 3.23 \quad \text{for } h < a < a_f$$

$$F_2(H) = \left[ 1 - \frac{9}{8}(H+1)^{-1} \right]^{-1} \quad \text{for } a < h < a_f$$

(9)

The external force component of the radial velocity consists of the van der Waals, electrical double layer and gravity forces. The London-van der Waals force was calculated using the equation due to Hamaker [17]:

$$F_{LO} = F_{ret} \frac{2}{3} \frac{A}{a} \frac{1}{(H+2)^2 H^2} \quad (10)$$

The electrical double layer was calculated

$$v_R = \frac{dH}{dt} = - \frac{F_1(H)}{6 \pi \mu a^2} \left\{ \begin{array}{l} 6 \pi \mu a^3 a_f^{-2} A_f U \cos \alpha_p F_2(H) + \\ \frac{2}{3} \frac{A}{a} \frac{F_{ret}}{(H+2)^2 H^2} + \frac{4}{3} \pi a^3 (\rho_p - \rho_f) g \cos \alpha_p \\ - \frac{\epsilon a \kappa (\Psi_1^2 + \Psi_2^2)}{2} \left[ \frac{2 \Psi_1 \Psi_2}{(\Psi_1^2 + \Psi_2^2)} - e^{(-\kappa h)} \right] \frac{e^{(-\kappa h)}}{(1 - e^{-2\kappa h})} \end{array} \right\} \quad (13)$$

The tangential velocity component of the particle consists of hydrodynamics and gravity contributions and is given by:

$$v_\alpha = \frac{d\alpha}{dt} = a a_f^{-1} A_f U \sin \alpha_p F_3(H) + \frac{4}{3} \pi a^3 (\rho_p - \rho_f) \frac{F_4(H)}{6 \pi \mu a} \quad (14)$$

In which  $F_3(H)$  and  $F_4(H)$  are the hydrodynamics correction factors.  $F_4(H)$  was taken as unity and  $F_3(H)$  was calculated by the relationship provided by Spielman [16]:

$$F_3(H) = \left[ \frac{0.7431}{(0.6376 - 0.2 \ln H)} \right] \quad \text{for } h < a < a_f$$

$$F_3(H) = \left[ 1 - \frac{5}{16}(H+1)^{-3} \right] \quad \text{for } a < h < a_f$$

(15)

using the equation by Hogg [18] for the interaction between a sphere and a plane:

$$F_{EDL} = \frac{\epsilon a \kappa (\Psi_1 + \Psi_2)}{2} \left[ \frac{2 \Psi_1 \Psi_2}{(\Psi_1^2 + \Psi_2^2)} - e^{(-\kappa h)} \right] \frac{e^{(-\kappa h)}}{1 - e^{(-2\kappa h)}} \quad (11)$$

Gravity contributes to both the tangential and the radial velocity components of the particle and its radial contribution is given by:

$$F_{Gr} = -\frac{4}{3} \pi a^3 (\rho_p - \rho_f) g \cos \alpha \quad (12)$$

Substituting expressions for the hydrodynamics, van der Waals, the electrical double layer, gravity forces, the radial velocity component of the particle is obtained as follows:

The trajectory equation was obtained by dividing equation (13) by (14):

$$\frac{-\sin \theta}{F_1} \frac{dH}{d\theta} = \frac{F_2 \cos \theta + N_G \cos \theta + N_{D1} (N_{D2} - N_{D3}) N_{D4} + N_{LO} \frac{F_{ret}}{(H+2)^2 H^2}}{F_3 + N_G \frac{a}{a_f}} \quad (16)$$

In this equation  $N_G$ ,  $N_{LO}$ ,  $N_{D1}$ ,  $N_{D2}$ ,  $N_{D3}$  and  $N_{D4}$  are dimensionless numbers representing the contribution of the gravity, London-van der Waals and electrical double layer respectively.  $H$  is the dimensionless distance ( $h/a$ ) of the particle from the collector surface.  $\theta$  is the angle made by the line joining the centers of the particle and the collector.  $F_1$ ,  $F_2$  and  $F_3$  are the hydrodynamic retardation factors taking into account the effect of the presence of particles in the vicinity of the collector.  $F_{ret}$  is the retardation factor in the equation for the calculation of the London-van der Waals force.

In experiments where no external potentials had been applied the zeta potential values have been used. As particles approach the collector, forces of gravity, London-van der Waals and hydrodynamics cause attraction between the surfaces, and for similarly charged surfaces the electrical double layer cause repulsion between surfaces.

Depending on the initial point of the approach of particles towards the surface they can either pass the collector or deposit on the surface of the collector. The concept of limiting trajectory was coined to divide the particle trajectories that end up in deposition from those that do not. The limiting trajectory makes an angle of  $180^\circ$  at the rear stagnation point of the collector as shown in Figure 5. To calculate the limiting trajectory, equation (16) is made equal to zero and the angle  $\theta$  equal to  $180^\circ$ . The root of the equation was estimated using the function ROOTS in Matlab. Figure 5 shows the limiting trajectory variation from the col

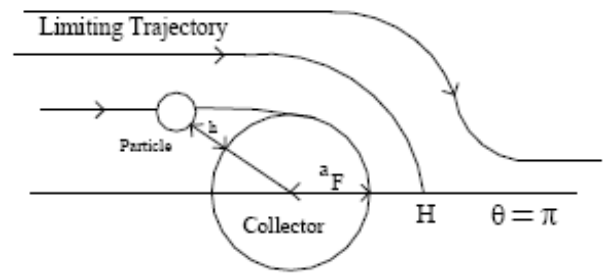


Figure 4. Location of limiting trajectory

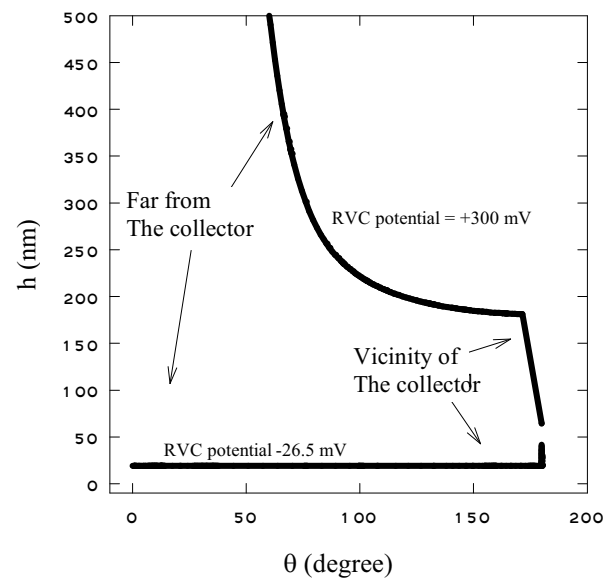


Figure 5. limiting trajectory for volumetric flowrate of  $34 \text{ cm}^3/\text{min}$  and RVC potential of  $+300 \text{ mV}$  and no external potential application (RVC zeta potential of  $-26.5 \text{ mV}$ )

lector surface carried out for the cases when the RVC collector potential is  $+300 \text{ mV}$ , and when no external applied potential has been applied, in which case the RVC's zeta

potential value was used. At all pH and electrolyte concentrations the polystyrene latex particles possess negative zeta potential values (see Bahmani [6] for details), and therefore at an RVC collector potential of +300 mV, attractive forces of interaction between polystyrene latex and the RVC collector exist. Particles at a distance of less than 46 nm from the rear stagnation point end up depositing on the collector surface, and particles at a distance greater than 46 nm from the rear stagnation point pass the collector surface.

Upon location of the limiting trajectory the filtration efficiency as given by Tien [19] is calculated from:

$$\eta = \frac{\Psi_{lim}}{u a_f} \quad (17)$$

In which  $\Psi_{lim}$  is the streamline of the limiting trajectory,  $u$  is the approach velocity and  $a_f$  is the collector radius. Theoretical filter coefficient can be calculated from the equation proposed by Tien [19]:

$$\lambda_{theo} = \frac{1}{L_C} \ln \left( \frac{1}{1-\eta} \right) = \frac{\eta}{L_C} \quad (18)$$

Experimental filter coefficient can be calculated from:

$$\ln \left( \frac{C_{in}}{C_{out}} \right) = \lambda_{exp} L \quad (19)$$

Before comparing simulation and experimental results, the effects of the variation of London-van der Waals and gravity on the filter coefficient and collection efficiency for the present system were studied. In these simulations all other forces such as electrical double layer and hydrodynamics were kept constant.

The simulation of the effect of the variation of the London-van der Waals force on the

filter coefficient as well as collection efficiency can be seen in figure 6. The London-van der Waals force was varied by using different Hamaker constants. Clearly as attractive London-van der Waals force increases, the collection efficiency and filter coefficient also increase.

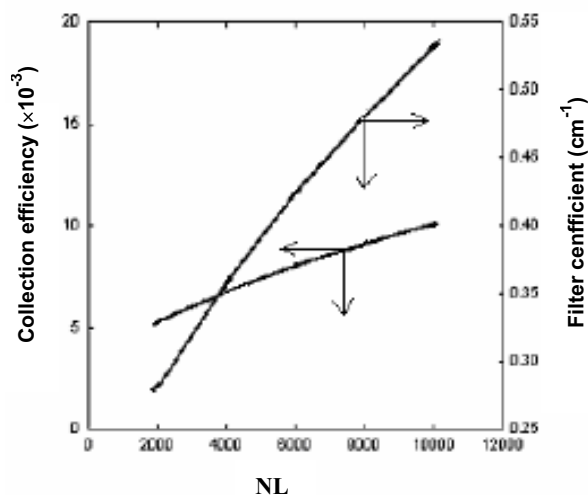


Figure 6. Simulation of Variation of collection efficiency and filter coefficient with van der Waals forces between particle and collector surfaces

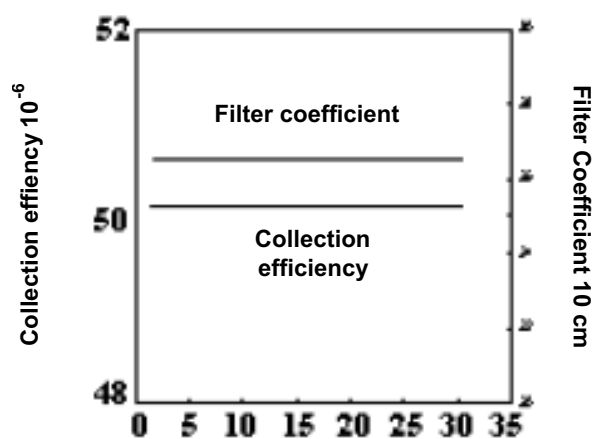
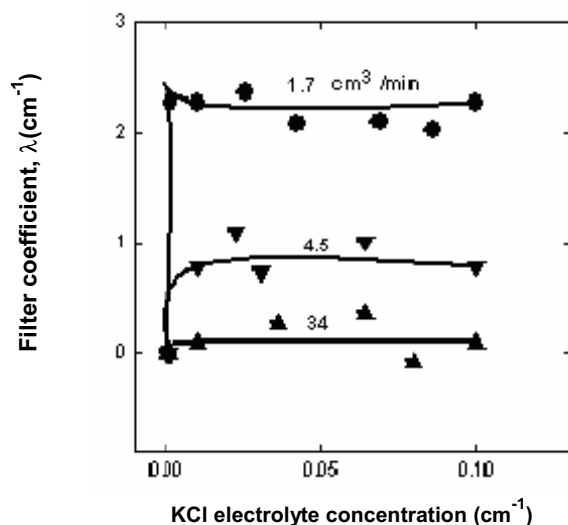


Figure 7. Simulation of variation of collection efficiency and filter coefficient with gravity number NG

The simulation of the effect of the variation of the gravity force on the filter coefficient

and collection efficiency can be seen in Figure 7. Clearly for the present system the gravity force has no effect on the deposition rate.

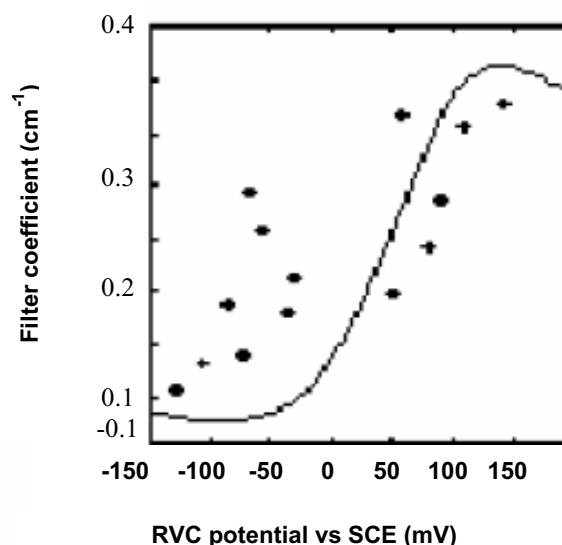
Figure 8 shows the comparison of simulation and experimental results at a constant RVC potential of +300 mV vs Standard Calomel Electrode (SCE). The experimental results indicate that a variation of the KCl electrolyte concentration at a fixed feed flowrate does not have a significant effect on the deposition rate, and simulation results also show a similar trend. This figure also shows that at the same RVC potential and KCl concentration, the reduction of feed flowrate from 34 to 1.7 cm<sup>3</sup> min<sup>-1</sup> increases the deposition rate. Indeed this is expected since lowering the feed flowrate increases the residence time of the particles, and hence a higher chance of deposition.



**Figure 8.** Comparison of simulation and experimental variation of filter coefficient with KCl electrolyte concentration at RVC potential of +300 mV

The main objective of the experiments carried out by Bahmani [6] has been to study the possibility of controlling the deposition rate by means of application of an external electric field to the collector. In equation (10) the external voltage applied to the collector was used for parameter  $\psi$ . Figure 9 shows a comparison between experimental and simu-

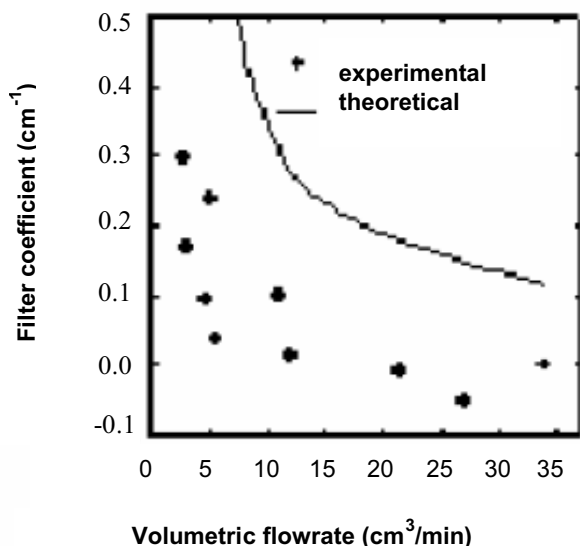
lation results for the variation of RVC electrode potential at a constant flowrate of 1.7 cm<sup>3</sup> min<sup>-1</sup>, KCl electrolyte concentration of 0.0001 mol dm<sup>-1</sup> and particle zeta potential value of -8.5 mV. Generally speaking, under favourable deposition conditions the simulation results predict the experimental results closely, but under unfavourable deposition conditions the simulations are not as good. Experimental results given by Bahmani [6] indicate that at collector potentials above 200 mV, a discharge of oxygen on the collector surface is observed. The discharge of oxygen may affect the deposition rate by changing the hydrodynamics and the pH of the solution. For example, the rising gas bubbles may exert enough drag force on the deposited particles to detach them or increase the resistance for the depositing particles. The electrolyte pH may be affected by the release of oxygen, which in turn affects the zeta potential values of the particles and collector.



**Figure 9.** Comparison of experimental and simulation results at constant KCl concentration of 0.0001 mol dm<sup>-1</sup>, flowrate of 1.7 cm<sup>3</sup> min<sup>-1</sup> and latex particle zeta potential of -8.5 mV

Figure 10 shows a comparison of experimental and simulation results for the variation of filter coefficient with feed

flowrate at constant RVC potential and KCl concentration. It can be concluded that the trend of the experimental results are well simulated.



**Figure 10.** Comparison of experimental and simulation results at fixed electrode potential of +300 mV and KCl concentration of 0.0001 0001 mol dm<sup>-1</sup>

### Conclusion

Experimental results previously reported by Bahmani [6] have been simulated using the trajectory analysis. For this system, gravity force does not have an important impact on the rate of deposition. Surface forces and the hydrodynamics are the major forces between the RVC collector and latex particles. At low flowrates the variation of surface forces affect the rate of deposition. Trends of the experimental results are well simulated by the trajectory analysis, but under an unfavourable deposition condition, wherein repulsive energy exists between collector and particle surface, discrepancy between simulation and experimental results are more evident.

In fact, discrepancy between simulation and experimental results under unfavourable deposition conditions has been noted as early as 1948 [2,20-22]. There have been several

theories put forward for this discrepancy such as; (1) in the trajectory analysis both collector and particle surfaces are assumed to have a uniform surface and surface charge, but in reality both surface and surface charge are heterogeneous, (2) existence of a secondary minimum as suggested by the total interaction energy (Figure 1) and capture of particles by the secondary minimum has been put forward for this discrepancy [7], (3) inclusion of other forces such as the hydrophobic, hydration, depletion [23] and other so called non-DLVO forces may improve simulations, (4) the correlation used for the estimation of the electrical double layer are based on the steady state overlap of the diffuse layers and additionally, the approximation of constant charge or constant potential during interaction is employed for the derivation of these correlations whereas in reality none of these are held constant during interaction [23].

### Nomenclature

- A Hamaker constant
- $a_f$  collector radius
- $C_{in}, C_{out}$  inlet and outlet particle concentration
- $F_{Lo}, F_{Gr}, F_{EDL}$  London-van der waals, gravity and electrical double layer forces
- $F_{ret}$  London van der Waals retardation factor
- h surface to surface separation distance
- H dimensionless gap (h/a)
- $L_C$  axial distance of a unit collector
- L total bed length

$$N_{LO} = \frac{Aa_f^2}{(9\pi\mu A_F U a^4)}$$

$$N_G = \frac{2a_f^2 g (\rho_p - \rho_f)}{9\mu U A_F}$$

$$N_{DI} = \frac{\epsilon k a_f^2 (\psi_1^2 + \psi_2^2)}{12\pi\mu a^2 A_F U}$$



$$N_{D2} = \frac{2\psi_1\psi_2}{\psi_1^2 + \psi_2^2}$$

$$N_{D3} = e^{-\kappa h}$$

$$N_{D4} = \frac{e^{-\kappa h}}{1 - e^{-2\kappa h}}$$

- U fluid bulk velocity  
 $\eta$  Single collector efficiency based on physical forces  
 $\epsilon$  Dielectric constant of the medium  
 $\kappa$  Debye-Huckel reciprocal length  
 $\psi_1, \psi_2$  surface potentials  
 $\lambda_{\text{theo}}, \lambda_{\text{exp}}$  theoretical and experimental filter coefficient

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