

# Removal of Surface Adhered Particles by Surfactants and Fluid Motions

Ashish Batra, Santanu Paria, C. Manohar, and Kartic C. Khilar

Dept. of Chemical Engineering, Indian Institute of Technology, Powai, Mumbai 400 076, India

*Removing or detaching particles from a surface is of interest in filter bed regeneration, cleaning of semiconductor surfaces, migration of fines in underground reservoirs, and detergency. A two-stage removal process proposed involves penetration of the surfactant solution, diffusion and adsorption of surfactant molecules, followed by the particle removal by hydrodynamic force. The particle-substrate system, considered here as a plate-plate system, takes into account the surface roughness of the substrate in the form of asperities. The concept of critical hydrodynamic force required to remove or detach a particle adhering to a substrate in the presence of surfactant solution is discussed, as well as its calculation of typical values. The critical hydrodynamic force depends on the surface roughness, particle size, and other parameters of the system. When asperity size is comparable to the equilibrium distance of separation, the critical hydrodynamic force becomes very large in magnitude, indicating that particle removal is very difficult. Higher critical hydrodynamic force is required for the removal of particles of small size.*

## Introduction

Removal or detachment of particles from adhering surfaces occurs in many industrial and domestic applications, such as detergency, cleaning of metal surfaces and regeneration of filter beds. This detachment problem is also of interest in areas ranging from enzyme fixation, adhesion on semiconductor surfaces, to migration of surface contaminants.

Detergency can be considered as a prototypical example of the problem of removal of particulate from adhering surfaces. It can be defined as the removal of unwanted substances from a solid surface immersed in a medium, generally through the application of a mechanical force, in the presence of a chemical substance (Kissa, 1987). The detachment and migration of fine particles in ground soil can cause soil and ground water pollution (Khilar and Fogler, 1998). Unconsolidated porous media are widely used in chemical engineering operations and processes such as filtration and packed-bed operations. When designing these operations, consideration needs to be given to prevent the occurrence of entrapment or plugging of the bed. For operations, such as regeneration of deep bed filters, a complete washout of the captured particles is required. Therefore, this problem of detachment of particles covers a wide gamut of engineering fields.

Here, we report a comprehensive analysis for the process of removal of particles by the actions of surfactants and fluid motions. The analysis is based on the Derjaguin Landau Verwey Overbeek theory and is extended with new modifications to account for some of the pertinent realistic conditions. The resulting changes in adherence conditions due to penetration of surfactant solution and adsorption of surfactant molecules are determined, taking into account the effects of surface roughness. The effect of fluid motion is incorporated into the total interaction energy to determine a critical hydrodynamic force above which the particle removal takes place. New and useful findings relating to the influences of important parameters on the critical hydrodynamic force are obtained and presented. The article focuses on detergency for its widespread applications. The findings, however, are applicable to particle removal processes in general under the action of fluid motion in presence of surfactants.

## Background Literature

### *Approach based on DLVO theory*

A theory by Lange (1967) is considered to belong to the category that has successfully discussed the removal of soil particles from the fabric surface, on the basis of the theory of

Correspondence concerning this article should be addressed to K. C. Khilar.

the stability of colloids developed independently by Derjaguin and Landau, as well as by Verwey and Overbeek, referred to for brevity as the DLVO theory. The total potential energy of interaction between the soil and fiber surface is calculated in these theories as the sum of the potential energy due to the electrical double layer repulsion and London van der Waals attraction.

For the sake of obtaining equations for various energies of interactions, the soil-textile system can be modeled as a plate-plate system (Lange, 1967). The interaction energy per unit area of van der Waals force between a plate-plate system is calculated by the equation described by (Hiemenz and Rajagopalan, 1997)

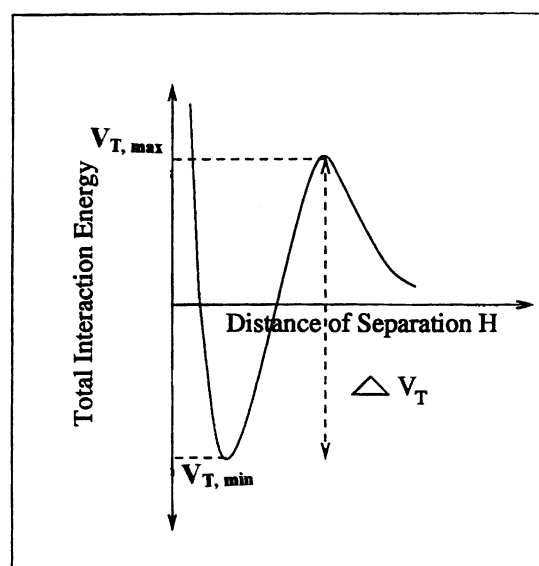
$$V_{LVA} = \frac{-A_{12}}{12\pi H^2} \quad (1)$$

where  $A_{12}$  is the Hamaker's constant for the fiber-soil system and  $H$  is the distance of separation between the fiber and soil. Particulate soil in the size range of 0.1–1  $\mu\text{m}$  is frequently unremovable by water alone, but is removable by detergent solutions. Such small particles generally adhere to smooth portions of fiber surface by van der Waals forces, which are too strong to be counteracted by hydrodynamic forces alone. When such a system is immersed in water, the energy of adhesion of the soil to the fiber is greatly altered, decreasing to about one-fourth of the original (Lange, 1967). This diminishing can be explained by a new Hamaker constant  $A_{123}$  for interaction of the fiber 1 and soil 2 in the water molecules 3. Hogg et al. (1966) calculated the potential energy of interaction between dissimilar flat double layers using the Debye-Huckel or linearized approximation. The energy of interaction per unit area is given by the equation

$$V_{DLR} = \frac{\epsilon\kappa}{2} \{ (\psi_1^2 + \psi_2^2) [1 - \coth(\kappa H)] + 2\psi_1\psi_2 \operatorname{cosech}(\kappa H) \} \quad (2)$$

where  $\psi_1$  and  $\psi_2$  are the zeta potentials of the plates 1 and 2, respectively,  $H$  is the distance of separation between the plates,  $\epsilon$  is the dielectric constant of the wash solution, and  $\kappa$  is the Debye-Huckel parameter. Typical values of zeta potentials of cotton and carbon-black in water and in a 0.4% detergent (heavy duty detergent based on sodium *n*-dodecylbenzenesulfonate and sodium tripolyphosphate) solution are –24 mV in water and –30 mV in the detergent solution for cotton, and –16 mV in water and –50 mV in the detergent solution for carbon black (Schott, 1972).

When the total interaction energy between the fiber and soil,  $V_T$  given by the sum of the interaction energy of the van der Waals interaction  $V_{LVA}$  and the interaction energy of the dissimilar electrical double layer, is plotted as a function of distance of separation, a typical plot looks as shown in Figure 1. When the surface potentials have the same sign,  $V_T$  is expected to reach a maximum at a certain distance where net attractive and repulsive force is zero. Higher zeta potential leads to higher  $V_{T\max}$ ; therefore, a high zeta potential should aid in detergency. Anionic surfactants are adsorbed onto



**Figure 1. Total potential energy curves for superposition of forces between fiber and soil particle (Mino, 1987).**

fibers and enhance the negative zeta potential, and, therefore, removal become easier. In case of low surfactant concentration, the addition of electrolytes promotes the adsorption of surfactant on the fiber and soil removal is increased, but after saturation of adsorption of surfactant, soil removal is decreased with electrolyte concentration.

#### Hydrodynamic effects and influence of surface roughness

A review article by Visser (1976) addresses the effects of hydrodynamic actions on an adhered particle. It has been pointed out that a tangential force  $F_t$ , due to the fluid drag, contributes to the dislodging force acting on the particle; however, the lift force contributes negligibly to the dislodging force. In the case of turbulent flows, the mechanism of detachment of colloidal particles from a flat substrate has been analyzed by Cleaver and Yates (1973). They have shown that a lift force exists due to the unsteady nature of the viscous sublayer in the turbulent boundary layer, and have proposed an equation to calculate this force.

Sharma et al. (1992) studied the influence of flow rate, particle size, particle elasticity, ionic strength, pH, and gravity on the detachment of colloidal particles. It shows the mechanism of detachment to be rolling, rather than sliding or lifting, for spherical particles on the flat surfaces.

Das et al. (1994) studied the effects of elastic deformation and surface roughness on the hydrodynamic detachment of colloidal particles from surfaces. They analyzed two limiting situations; in one, a rigid sphere on a deformable substrate and, in the other, a deformable sphere on a rigid substrate. They concluded that, to release a rigid spherical particle from a deformable substrate, the hydrodynamic force required is infinitesimally small. In the case of a deformable particle interacting with a rigid substrate, the deformation caused by the action of a hydrodynamic force is negligibly small and,

therefore, does not provide a large enough restraining torque. They also concluded that surface roughness is a necessary condition for existence of a large enough restraining torque that may balance the imposed hydrodynamic force.

In a study to understand the deposition of latex spheres onto textile fibers, it was found that latex spheres usually deposited along grooves in the fibers (Tamai et al., 1983). This deposition pattern, as well as discrepancies between the experimental results and predictions based on a model of spherical particles and a flat plate, led to a conclusion that surface features significantly affect the interaction energies between particles. The effect of surface roughness on the van der Waals interactions of contacting agglomerates of particles has also been studied (Czarnecki, 1986).

### **Particle release conditions**

In a study addressing the release of fine particles in sandstones, Khilar and Fogler (1984) proposed that the release of fine particles may begin at a specific salt concentration at which the total energy and total force acting on the particle are zero. They also experimentally found the existence of such a critical salt concentration. In the case of the release of particles in turbulent flow, Cleaver and Yates (1973) have shown that there exists a minimum wall shear stress for release and that magnitude is dependent on the particle size. In cases of flow through soil masses and sandstone formations, the existence of a critical shear stress or velocity has been found experimentally (Arulanandan et al., 1975).

In this study, we have carried out a systematic analysis for the particle removal process induced by fluid motion in presence of surfactant species. The influence of various pertinent parameters, such as the surface roughness, the nature of surfactant, particle size, and so on, have been determined.

### **Proposed Mechanism**

We consider the mechanism of removal of particles as a two-stage process, as described below. The mechanism will be described for fiber-soil particle systems, keeping in mind the importance of detergency. However, the mechanism can be applied to any substrate-particle system in its general form.

#### **Stage 1: surfactant diffusion and adsorption**

In stage one, the phenomenon of diffusion of the surfactant molecules followed by adsorption onto the substrate occurs. For the adsorption of surfactants to take place, the surfactant solution must penetrate into the constricted space through the capillary systems on the fiber or the soil.

Fabrics are composed of three capillary systems: capillaries between threads, capillaries between the fiber of each thread, and capillaries between the fibrils of each fiber. When we talk of penetration of solution in the space between the fabric and the soil, three cases may be considered.

- Hydrophobic fabric-hydrophobic soil: in this case an aqueous surfactant solution will penetrate only through the slit between the flat surface of the fiber and soil and the time of penetration can be estimated based on the Washburn (1921) equation.

- Hydrophilic fabric-hydrophobic soil: in this case the surfactant solution can move through the vertical capillaries

and/or the horizontal capillaries between the fibers as described by the Washburn (1921) equation and then spread radially through the capillaries as described in the radial capillary model developed by Marmur (1988).

- Hydrophilic fabric-hydrophilic soil: the surfactant solution can move through the vertical capillaries on both the substrates and time of penetration can be estimated by the Washburn (1921) equation and the radial capillary equation by Marmur (1988).

It is believed that, in most cases, the penetration between the soil particles and the fiber is critical to the removal process of the particle. It is to be noted that this penetration process is related to the kinetics of removal process and sufficient time needs to be allowed for the wetting and penetration of surfactant solution to take place.

In the mechanism of detergent action, adsorption of surfactants plays an important role. Kinetic models for surfactant adsorption processes consists of two steps. The first step is the transport of the surfactant to the subsurface of fibers or soil, driven by concentration gradient or hydrodynamic forces. The second step is the surfactant molecules from the surface to the adsorbed state. Usually the second step is rapid and the first step determines the adsorption rate, especially when the transport of the surfactant molecule is governed by diffusion. For solute such as surfactant molecules that are large enough to behave as hydrodynamic particles, the phenomena of hindered diffusion occurs in the constrained space between the fiber and the particle. As a result, the concentration inside the constricted space is different from the adjacent bulk concentration. Therefore, what is needed is a partition coefficient that is able to relate the concentration of the surfactant in the constricted space between soil and the fiber that may be modeled as a flat slit system to the bulk concentration. This in turn can be related to the zeta potential that develops on the surface due to surfactant adsorption.

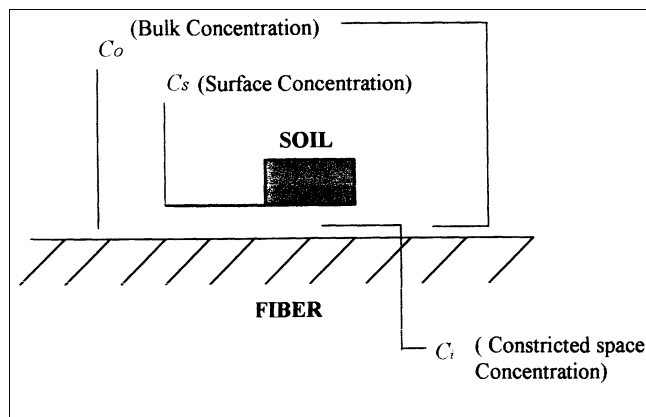
#### **Stage 2: removal of particles by fluid action**

After the ionic surfactant molecules adsorbed onto the surfaces, zeta potential develops on these surfaces which leads to a repulsive double layer interaction between them. Also, in the presence of surfactant species, the van der Waals attraction between the fiber and the particle also decreases. Thus, the adherence of the particle to the substrate is considerably weakened. It is being proposed that a lift force generated due to the turbulence in a highly agitated system, such as a washing machine or other device, can cause the now weakly adhering particle to be detached from the surface. The removal has been characterized in terms of a critical hydrodynamic force. Hydrodynamic force above this critical value may cause the removal/detachment of the adhering particle.

### **Analysis Formulation**

#### **Stage 1: surfactant diffusion and adsorption**

We consider the constricted space as shown in Figure 2. We further identify and define three concentrations:  $c_o$  the bulk concentration of the surfactant solution,  $c_i$  the concentration inside the constricted space, and  $c_s$  the surface concentration.



**Figure 2. Constricted space and different concentrations in a particle-fiber system.**

The partition coefficient  $\Phi$  may be defined as the ratio of the cross-sectional average concentration  $\langle c_i \rangle$  at either end in the constricted space to the bulk solution  $c_o$  (Deen, 1987). This partition coefficient can arise due to pure steric considerations and also due to the electrostatic interactions between the pore wall and the diffusing surfactant molecule, and is a function of  $\lambda^*$ , the ratio of the radius of the solute to the width of the pore.

An adsorption coefficient  $K$  can be defined as the ratio of  $\langle c_s \rangle$ , the average surface concentration and  $\langle c_i \rangle$ , the average concentration in the constricted space. The value for the adsorption coefficient  $K$  is expected to be different for particle and for the substrate. Now we can relate the surface charge to the zeta potential (when the zeta potential is small) by the simple capacitor equation, assuming small values for the

potential

$$\psi = \frac{\sigma^*}{\epsilon \times \kappa} \quad (3)$$

The surface charge density  $\sigma^*$  is given after expressing in terms of bulk concentration  $c_o$

$$\sigma^* = 96,500 \times K \times \Phi \times c_o \quad (4)$$

where  $\kappa$  is

$$\frac{1}{\kappa} = \sqrt{\frac{\epsilon k_B T}{2,000 e^2 N_A \times c_i}} \quad (5)$$

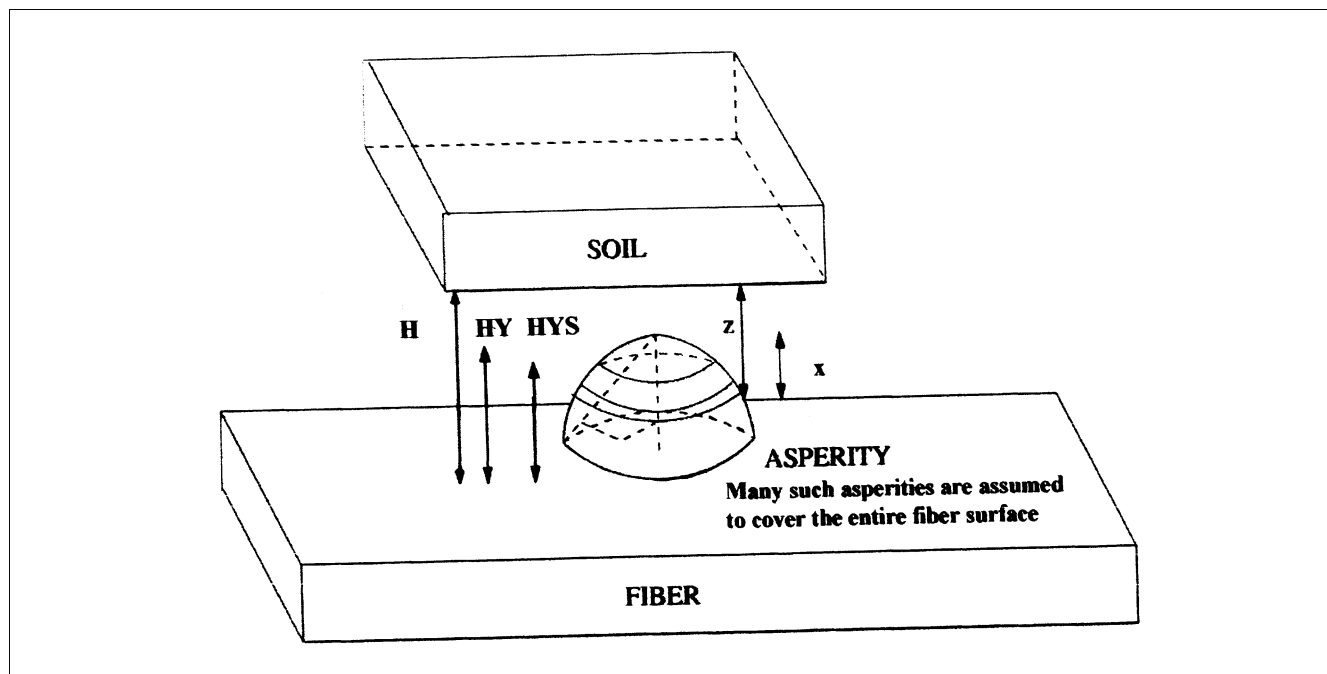
Electrostatic interactions between the pore wall and the surfactant molecule (sphere-plate system) are assumed to be constituted by double layer repulsion (Hogg et al., 1966), van der Waals attraction (Hunter, 1989) and Born repulsion (Ruckenstein and Prieve, 1976).

### Stage 2: removal of particles by fluid action

We can write the appropriate equations for the van der Waals, double layer, and other energy of interactions. The geometry of the system is shown in Figure 3.

The expressions for the van der Waals interaction of one hemispherical asperity with the block opposite is given as (Herman and Papadopoulos, 1990)

$$V_{LVA} = \frac{-A_{123}}{6} \int_{D(1-s)}^D \frac{x D (\tan^2 \theta + 1) - x^2}{(H - D + x)^3} dx + \frac{-A_{123}}{6} \int_H^\infty \frac{D^2 \tan^2 \theta}{z^3} dz \quad (6)$$



**Figure 3. Fiber-soil system as a platelet-plate system with hemispherical asperities mounted on the fiber for the entire area to be covered.**

For a finite area, the number of asperities can be easily calculated and the total van der Waals interaction of the block can be found by multiplying the above equations by the number of asperities in that area.

The expression for one hemispherical asperity with the block opposite it for the double layer interaction is given as (Herman and Papadopoulos, 1990)

$$V_{DLR} = \int_{D(1-s)}^D \frac{\epsilon\kappa}{2} \{ (\psi_1^2 + \psi_2^2) [1 - \coth(\kappa(x + H - D))] + 2\psi_1\psi_2 \operatorname{cosech}[\kappa(x + H - D)] \} dx \quad (7)$$

An equation for the energy due to AB interaction is given as (Chedda et al., 1992)

$$V_{AB} = \mp V_{AB}^0 \exp\left(\frac{-(H - H_o)}{\lambda}\right) \quad (8)$$

Here  $V_{AB}^0$  = hydrophobic interaction in J/m<sup>2</sup>,  $H_o$  = minimum equilibrium distance in m, and  $\lambda$  = decay length of liquid molecules, in m. The negative sign implies hydrophilic attraction, and the positive sign hydrophilic repulsion. This equation is valid for the solid liquid system. Taking water as the liquid, reasonable values for  $H_o$  and  $\lambda$  are 0.5 nm and 1.0 nm, respectively. Typical values of  $V_{AB}^0$  may be a few tens to few hundreds of  $k_B T$ .

Feke et al. (1984) using the repulsive part of the Lennard-Jones potential and adopting the Hamaker procedure of pairwise additivity and integration have developed an equation for Born repulsion potential for two identical spheres. However, here, an expression has been adopted for the plate-plate case (Sharma et al., 1992)

$$V_{BR} = \frac{A_{123}\sigma^6}{360H^8} \quad (9)$$

It may be noted that the cleaning or removal of particles in many industrial or domestic applications is done in turbulent flow conditions. In a washing machine, due to repeated changes in direction of the agitator, it is expected that the flow would be in the turbulent regime. Furthermore, if particles are not perfectly spherical, lift force of hydrodynamic origin may exist. We therefore need to identify any lift force acting on a particle resting on a surface and subjected to turbulent flows. Cleaver and Yates (1973) have addressed this issue and have shown that there is a good possibility of lift force acting on the particle generated due to the unsteady nature of various sublayer arising out of sudden frequent bursts of turbulent eddies. Another source of generation of lift force would be a common effect related to the asymmetric nature of flows.

This lift force acts normal to the surface and, hence, can be added to the other force such as van der Waals and double layer force. Cleaver and Yates has proposed the equation

to calculate this force

$$F_H = 0.076 \rho \nu^2 \left( \frac{2Rv}{\nu} \right)^3 \quad (10)$$

Assuming constant force for small distance of separation, the hydrodynamic energy of interaction  $V_{HR}$  is given as

$$V_{HR} = 0.076 \rho \nu^2 \left( \frac{2Rv}{\nu} \right)^3 \times H \quad (11)$$

where  $H$  is the distance of separation.

The total interaction energy,  $V_T$  is obtained by adding algebraically the various components

$$V_T(H, R, A_{132}, \rho, \nu, v, \sigma, \psi_1, \psi_2, c_o, \pm V_{AB}^0) = (V_{DLR} + V_{LVA} + V_{BR} + V_{AB}) \times a + V_{HR} \quad (12)$$

Here  $a$  is the area of the adhered particle in m<sup>2</sup>.

Using a concept analogous to critical flocculation concentrations (CFC); or critical salt concentration; (CSC), we define the critical hydrodynamic force, as the hydrodynamic force at which both the total interaction energy and total force vanish. Mathematically

$$V_T = 0 \quad (13)$$

$$-\frac{dV_T}{dH} = 0 \quad (14)$$

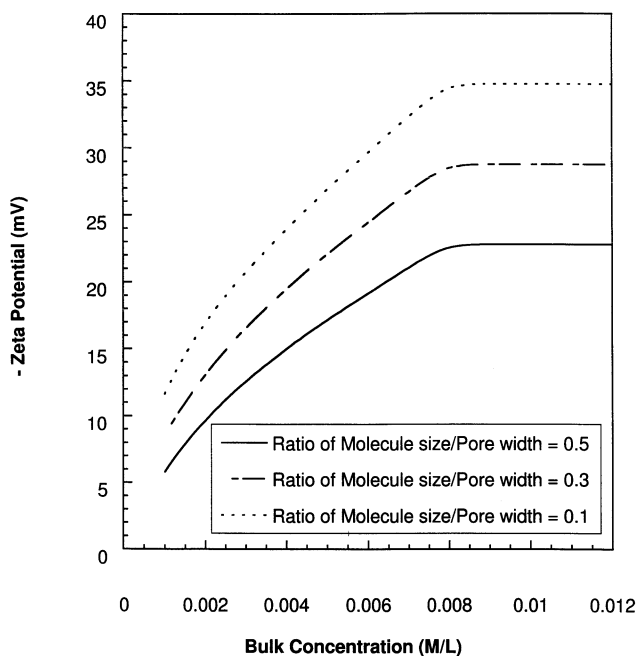
Under a given condition, a particle may be detached when the hydrodynamic force is greater than the critical hydrodynamic force.

## Result and Discussions

### Adsorption of ionic surfactants and zeta potential

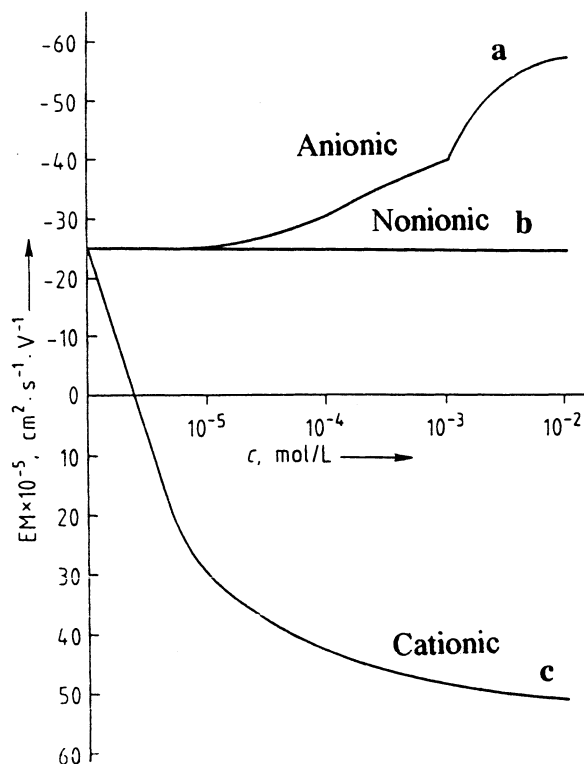
Figure 4 represents the values of zeta potential calculated as a function of bulk concentration of surfactant. We observe from this figure that the zeta potential increases with an increase in the bulk concentration of the surfactant. Importantly, the size of the surfactant molecule has significant effects on the zeta potential. It is also noted that beyond the critical micelle concentration (CMC) of the surfactant, the bulk concentration remains at the CMC, and, hence, the extent of adsorption and the resulting zeta potential do not increase beyond the CMC. As a characteristic example of an anionic surfactant, SDS which has a CMC of 8 mM has been considered, and, therefore, zeta potential continues to increase until a concentration of 8 mM and then levels off at the value of zeta potential at 8 mM.

These observations compare well with the experimental trends of zeta potential as shown by Jakobi and Löhr (1987). Figure 5 presents these results in terms of the electrophoretic mobility of carbon black in the presence of anionic, cationic, and nonionic surfactants, which show the leveling off the zeta potential beyond the CMC. We observe here that zeta potential levels off beyond a particular concentration, which is comparable to the CMC of the surfactant. As a matter of fact, there are reported studies that show that the adsorption of surfactants, in general, decreases beyond CMC due to sol-

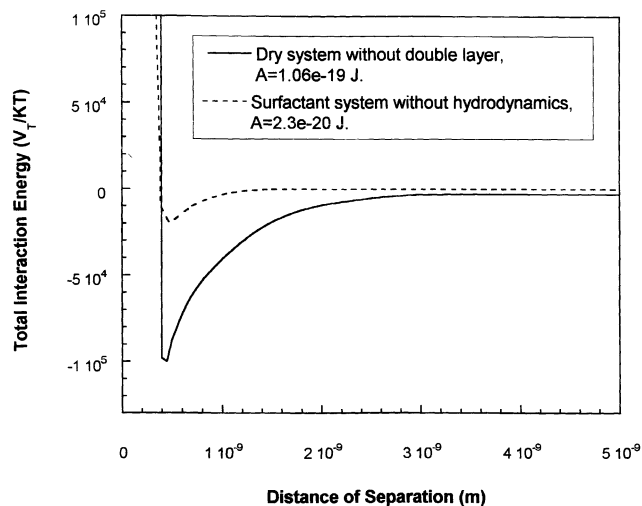


**Figure 4. Zeta potential vs. bulk concentration of SDS at various radius of molecule size/width of slit pore (steric and electrostatic interactions).**

ubilization of short chain molecules (Furst et al., 1996). Considering that the actions are taking place inside the con-



**Figure 5. Electrophoretic mobility of carbon black.**  
(a) Anionic surfactant; (b) nonionic, (c) cationic (Jacobi and Löhr, 1987).



**Figure 6. Transition from a dry particle-fiber system to a fiber system.**

stricted space, it is reasonable to assume that the adsorption and zeta potential both level off beyond the CMC of the surfactant.

#### *Energy curve of dry and wet systems*

Figure 6 represents the transition from a dry fiber-soil system to a wet fiber-soil system. The total interaction energy of a dry soil and fiber system is constituted by the van der Waals attraction energy, AB interactions and Born repulsion, but no electrostatic double layer repulsion. The value of Hamaker's constant for the system of Nylon- $\text{Al}_2\text{O}_3$  was considered as a characteristic value for a dry fiber-soil system. In the presence of a surfactant solution, double layer repulsion and a reduced value of Hamaker's constant for a Nylon-Water- $\text{Al}_2\text{O}_3$  (a reduction almost 80%) weakened the adherence of the soil to the fiber. Water might also be acting by allowing surface groups on both substrates to become charged due to its high dielectric constant and, hence, allowing the electrostatic repulsion to lower the adherence of the particle. Note the primary minimum that shifts from a higher negative value in a dry system to a less negative value in the wet system. The very high values of the total interaction energy can be attributed to the very small equilibrium distance of separation.

#### *Critical hydrodynamic force*

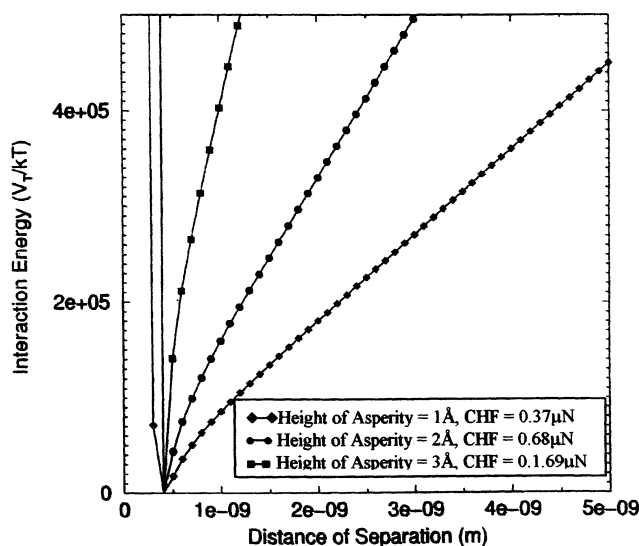
The critical hydrodynamic force is defined as the minimum force required to detach the particle from the fiber under a given condition. The critical hydrodynamic force is calculated for different conditions. The range of parameters used are shown in Table 1. In all the plots considered in this article the equivalent radius of a soil particle has been considered as  $0.1 \mu\text{m}$ .

*Influence of Asperities.* Figure 7 shows the plots of total interaction energy at different values for the heights of asperities. At the equilibrium distance of separation, with the critical hydrodynamic energy, the total energy of interactions be-

**Table 1. Parameters Used in the Critical Hydrodynamic Force Calculations**

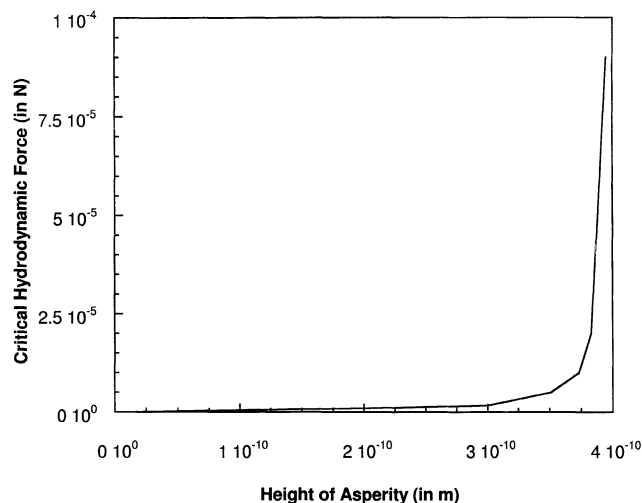
Parameter	Range
Hamaker's Constant $A$	$2 \times 10^{-20} \text{ J}$ to $1 \times 10^{-19} \text{ J}$
Zeta Potential of Soil $\psi_1$	$-20 \text{ mV}$ to $-50 \text{ mV}$
Zeta Potential of Fabric $\psi_2$	$-40 \text{ mV}$ to $-70 \text{ mV}$
Hydrophobic Interaction $V_{AB}^0$	$-1,000 k_B T$ to $1,000 k_B T$
Conc. of surfactant and electrolyte	$0.001 \text{ M}$ to $0.02 \text{ M}$
Adsorption Coefficient	$0.01$

comes zero. The very large values of the total interaction energy may be attributed to the very small equilibrium distance of separation possible for the extremely small size of the particles. Figure 8 presents the critical hydrodynamic force at different values of asperities. We observe from this plot that the critical hydrodynamic force increases with the height of asperities. Significantly, as the height of asperity becomes comparable to that of the equilibrium distance, critical hydrodynamic force increases steeply and is found to asymptotically approach a very large value of force for an asperity height of  $\text{\AA}$ , equal to the equilibrium distance of separation. When the asperity height becomes comparable to that of the equilibrium distance of separation between the fiber and soil, the distance of separation between the particle and asperities becomes extremely low, and the interactions are very strong, and, therefore, force required to dislodge the particle is very high. Therefore, the importance of modeling with asperities lies more in studying particles not simply adhering, but trapped, between the pores of the fabric. It may also be noted that the presence of asperities does not significantly alter the volume of the fiber and, hence, comparisons between the smooth plate model and the model with asperities are unambiguous.



**Figure 7. Potential energy curve at different asperity heights.**

$A = 2.326 \times 10^{-20} \text{ J}$ ,  $\psi_1 = -50 \text{ mV}$ ,  $\psi_2 = -30 \text{ mV}$ ,  $\kappa = 4.64 \times 10^8 \text{ m}^{-1}$  for the rough platelet-plate model at critical velocities.



**Figure 8. Critical hydrodynamic force vs. height of the asperity.**

$V_{AB}^0 = -4.14 \times 10^{-18} \text{ J/m}^2$ ,  $\psi_1 = -50 \text{ mV}$ ,  $\psi_2 = -30 \text{ mV}$ ,  $\kappa = 4.64 \times 10^8 \text{ m}^{-1}$  for the rough platelet-plate model.

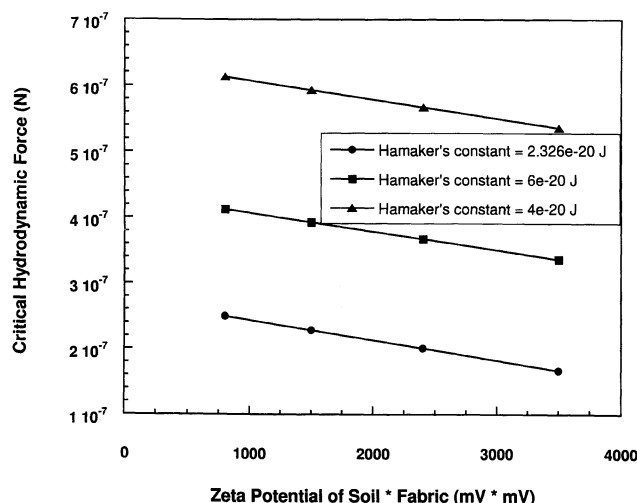
### *Influence of Zeta Potential and Hamaker's Constant*

Figure 9 presents the variation in critical hydrodynamic force with zeta potentials. We observe from this figure that an increase in the zeta potential of either fiber or the soil reduces the critical hydrodynamic force. An anionic surfactant increases the zeta potentials of the fabric and the soil and, hence, it is expected that the critical hydrodynamic force should decrease on addition of surfactant. The zeta potential has been made to vary over the range in water solution to surfactant solution.

With an increase in the Hamaker's constant, the critical hydrodynamic force increases. This is also expected since Hamaker's constant is a measure of the strength of the van der Waals force of attraction which binds the particle to the surface. For strongly adhered particles, more energy must be expended to remove it. The Hamaker's constant has been made to vary from the value of Nylon- $\text{Al}_2\text{O}_3$ -Water ( $\sim 2 \times 10^{-20} \text{ J}$ ) to Nylon- $\text{Al}_2\text{O}_3$ -Air system ( $\sim 1 \times 10^{-19} \text{ J}$ ).

**Influence of Particle Size.** Figure 10 presents the variations in critical hydrodynamic force with the size of the particles. We can observe from this figure that as particle size increases, the critical hydrodynamic force increases due to an increase in the area of the particle, but the critical velocity (by backcalculating from the expression of hydrodynamic force) decreases with increasing in particle size. This corresponds to the critical hydrodynamic forces shown in Figure 10. This velocity can range from  $72 \text{ m/s}$  for a particle of size  $0.1 \text{ }\mu\text{m}$  to a velocity of  $7 \text{ m/s}$  for a particle size of  $100 \text{ }\mu\text{m}$  and  $9 \text{ m/s}$  for a particle size of  $50 \text{ }\mu\text{m}$ . Typical velocities in a washing and cleaning device would never exceed  $10 \text{ m/s}$ . This observation validates the fact that extremely small particles would never be removed by only mechanical action of cleaning in washing devices. Other modes of cleanings are necessary in these cases.

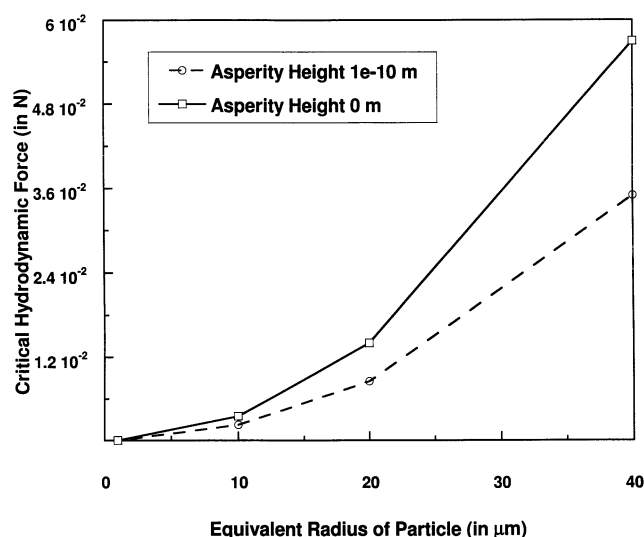
Sharma et al. (1992) reported that the critical hydrodynamic force increases with increasing the particle sizes. While there is a qualitative agreement between our calculations and



**Figure 9. Critical hydrodynamic force vs. product of the zeta potentials of fiber and soil.**

$V_{AB}^0 = -4.14 \times 10^{-18} \text{ J/m}^2$ , asperity height = 0 and  $\kappa = 4.64 \times 10^8 \text{ m}^{-1}$  at different values of Hamaker's constant.

those of Sharma et al. (1992) quantitatively our calculations show much higher values for critical hydrodynamic force. This is due to the fact that we have taken a platelet-plate system of considerable area of contact, lower equilibrium distance of separation, and presence of asperities on the substrate surface. Furthermore, we have considered lift as the mechanism of removal for these platelet shaped particles trapped in grooves of the surface. All these characteristics of our system model the realities of nonspherical particles trapped in the grooves of the surface to which it is adhered. Under these conditions, the adhesion force is significantly higher and therefore, the critical hydrodynamic force is higher. There is no reported data using a system closely resembling to the particle situations that we have considered. However, we be-



**Figure 10. Critical hydrodynamic force vs. equivalent radius of the particle.**

lieve our calculated force may be on the higher side because of a extremely small equilibrium distance of separation. Therefore, our calculations provide an upper bound to the critical hydrodynamic force. At the same time, it is interesting to note that for large size particles, the calculated velocity compares well with the typical velocity prevailing in washing machines.

## Conclusions

Hindered diffusion of the surfactant and subsequent adsorption develops zeta potential on both surfaces. The critical micelle concentration of the surfactant has been found to control the maximum zeta potential that can develop on a surface.

Once the surfaces acquire a surface charge as a result of the ionic surfactant adsorption, then, due to the electrostatic double layer repulsions between the two surfaces and the reduced Hamaker's constant, the adherence of the particle weakens and hydrodynamic forces then cause this particle to be removed. A critical hydrodynamic force can be defined beyond which the particle can be detached.

The magnitude of critical hydrodynamic force is dependent on the zeta potential, particle size, and on the surface roughness. It is shown that the smaller the particle size, the larger the requirement of critical hydrodynamic force, which is strongly dependent on the presence of roughness on the surface. Significantly, as the height of the surface asperities becomes comparable to the equilibrium distance of separation between the fiber and soil, it can become virtually impossible to dislodge the particle. This finding provides a reason as to why cleaning is very difficult in some situations and is potentially useful to generate new techniques for difficult cleaning.

## Acknowledgment

The authors gratefully acknowledge the financial support of Unilever Industries Pvt. Ltd., Bangalore, India, to carry out this work. The authors wish to thank Drs. Peter Garrett and Girish Rao of Unilever Research Center, Bangalore, for many stimulating discussions on this topic. The authors thank the reviewers for some good suggestions.

## Notation

- $A_{123}$  = Hamaker's constant for a fiber-soil-liquid system, J
- $A_{12}$  = Hamaker's constant for a fiber-soil system, J
- $a$  = area of particle,  $\text{m}^2$
- $c_i$  = concentration in the constricted space, M/L
- $c_s$  = surface concentration,  $\text{gmol/m}^2$
- $c_o$  = bulk concentration, M/L
- $D$  = height of asperity, m
- $e$  = electronic charge,  $1.6 \times 10^{-19} \text{ C}$
- $F_H$  = hydrodynamic force, N
- $H$  = distance of separation, m
- $H_o$  = minimum equilibrium distance, m
- $k_B$  = Boltzmann constant,  $\text{J} \cdot \text{K}^{-1}$
- $K$  = adsorption coefficient, m
- $N_A$  = Avagadro's Number, dimensionless
- $R$  = radius of the particle, m
- $T$  = temperature, K



$V_{LVA}$  = interaction energy due to van der Waals attraction,  $J \cdot m^{-2}$   
 $V_{DLR}$  = interaction energy due to double layer repulsion,  $J \cdot m^{-2}$   
 $V_{AB}$  = interaction energy due to AB interactions,  $J \cdot m^{-2}$   
 $V_{AB}^o$  = hydrophobic interaction  
 $V_{HR}$  = hydrodynamic energy, J  
 $V_{BR}$  = interaction energy due to Born Repulsion,  $J \cdot m^{-2}$   
 $V_T$  = total interaction energy, J  
 $\psi_1$  = zeta potential of soil, mV  
 $\psi_2$  = zeta potential of fabric, mV  
 $\epsilon$  = dielectric constant,  $J^{-1} \cdot C^2 \cdot m^{-1}$   
 $\theta$  = angle of asperity, degree  
 $\kappa$  = Debye-Huckel parameter,  $m^{-1}$   
 $\lambda$  = decay length, m  
 $\lambda^*$  = ratio of molecule size to pore dimension, dimensionless  
 $\rho$  = density of wash solution,  $kg \cdot m^{-3}$   
 $\sigma$  = atomic collision diameter, m  
 $\sigma^*$  = surface charge density,  $C \cdot m^{-2}$   
 $v$  = velocity of fluid,  $m \cdot s^{-1}$   
 $\nu$  = kinematics viscosity,  $m^2 \cdot s^{-1}$   
 $\Phi$  = partition coefficient, dimensionless

## Literature Cited

- Arulanandan, K., P. Loganathan, and R. B. Krone, "Prone and Eroding Fluid Influences on Surface Erosion of Soil," *J. Geotechnol. Eng. Div.*, ASCE, **101**, 51 (1975).
- Chedda, P., D. Grasso, and C. J. Van Oss, "Impact of Ozone on Stability of Montmorillonite Suspensions," *J. Colloid Interface Sci.*, **153**, 226 (1992).
- Cleaver, J. W., and B. Yates, "Mechanism of Detachment of Colloidal Particles from a Flat Substrate in a Turbulent Flow," *J. Colloid Interface Sci.*, **44**, 464 (1973).
- Czarnecki, J., "The Effects of Surface Inhomogeneities on the Interactions in Colloidal Systems and Colloid Stability," *Adv. Colloid Interface Sci.*, **24**, 283 (1986).
- Das, S. K., R. S. Schechter, and M. M. Sharma, "The Role of Surface Roughness and Contact Deformation on the Hydrodynamic Detachment of Particles from Surface," *J. Colloid Interface Sci.*, **164**, 63 (1994).
- Deen, W. M., "Hindered Transport of Large Molecules in Liquid Field Pores," *AIChE J.*, **33**, 1409 (1987).
- Feke, D. L., N. D. Prabhu, J. R. Mann, Jr., and J. R. Mann, III, "A Formulation of the Short Range Repulsion between Spherical Colloidal Particles," *J. Phys. Chem.*, **88**, 5735 (1984).
- Furst, E. M., E. S. Pagac, and R. D. Tilton, "Coadsorption of Polylysine and the Cationic Surfactant Cetyltrimethylammonium Bromide on Silica," *Ind. Eng. Chem. Res.*, **35**, 1566 (1996).
- Herman, M. C., and K. D. Papadopoulos, "Effects of Asperities on the van der Waals and Electric Double-Layer Interactions of Two Parallel Flat Plates," *J. Colloid Interface Sci.*, **136**, 385 (1990).
- Hiemenz, P. C., and R. Rajagopalan, *Principles of Colloid and Surface Chemistry*, Chapter 10, Marcel Dekker, New York (1997).
- Hogg, R., T. W. Healy, and D. W. Fuerstenau, "Mutual Coagulation of Colloidal Dispersions," *Trans. Faraday Soc.*, **62**, 1638 (1966).
- Hunter, R. J., *Foundations of Colloid Science*, Vol. 1, Chapter 4, Oxford Univ. Press, (1989).
- Jakobi, G., and A. Löhr, "Theory of the Washing Process," *Detergent and Textile Washing-Principles and Practice*, Chap. 2, VCH, Germany (1987).
- Khilar, K. C., and H. C. Fogler, "The Existence of a Critical Salt Concentration for Particle Release," *J. Colloid Interface Sci.*, **101**, 214 (1984).
- Khilar, K. C., and H. C. Fogler, *Migration of Fines in Porous Media*, Chapter 1, Kluwer Academic Publishers, Netherlands (1998).
- Kissa, E., "Evaluation of Detergency," *Detergency: Theory and Technology*, W. G. Cutler, and E. Kissa, eds., Chapter 1, Marcel Dekker, New York (1987).
- Lange, H., "Physical Chemistry of Cleaning Action," *Solvent Properties of Surfactant Solutions*, K. Shinoda, ed., Marcel Dekker, New York, p. 117 (1967).
- Marmur, A., "The Radial Capillary," *J. Colloid Interface Sci.*, **124**, 301 (1988).
- Mino, J., "Detergency Advances in Japan," *Detergency: Theory and Technology*, W. G. Cutler, and E. Kissa, eds., Chapter 9, Marcel Dekker, New York (1987).
- Ruckenstein, E., and D. C. Prieve, "Optimum Pore Size for the Catalytic Conversion of Large Molecules," *AIChE J.*, **22**, 276 (1976).
- Schott, H., "Removal of Particulate Soil," *Detergency Part 1*, W. G. Cutler, and R. C. Davis, eds., Chapter 6, Marcel Dekker, New York (1972).
- Sharma, M. M., H. Chamoun, D. S. H. R. S. R. Sarma, and R. S. Schechter, "Factors Controlling the Hydrodynamic Detachment of Particles from Surfaces," *J. Colloid Interface Sci.*, **149**, 121 (1992).
- Tamai, H., Y. Nagai, and T. Suzawa, "Latex Deposition on Fibers VI. Deposition State and Interaction Energy," *J. Colloid Interface Sci.*, **91**, 464 (1983).
- Visser, J., "Adhesion of Colloidal Particles," *Surface and Colloid Sci.*, E. Matijevic, ed., Chapter 1, Wiley, New York (1976).
- Washburn, E. W., "The Dynamics of Capillary Flow," *Phys. Rev.*, **27**, 273 (1921).

Manuscript received Aug. 30, 2000, and revision received Apr. 2, 2001.