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Effect of physicochemical and hydrodynamic conditions on kinetics of carbon particles deposition on plastic particles

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Abstract

Deposition of carbon particles on plastic spheres was experimentally investigated. The effects of $CaCl_2$ concentration, soap concentration and the mixing speed on the deposition rate and the equilibrium particle concentration were studied. The effect of the above parameters on the Langmuir model constants was also determined.

In the absence of $CaCl_2$, almost no deposition takes place. However, when $CaCl_2$ was added, the deposition becomes very fast. A large equilibrium constant was obtained when the concentration of $CaCl_2$ equals the stoichiometric amount necessary to react with the sodium stearate soap. On the other hand, when the concentration of $CaCl_2$ was above the stoichiometric amount, both coagulation of carbon particles and deposition took place simultaneously. When the soap concentration was above the stoichiometric amount the deposition rate is slow. Further increase in the soap concentration has similar effect on the deposition rate.

The effect of mixing speed on the deposition rate was examined. Mixing speeds of 100, 300 and 500 rpm were used. Results showed that the deposition rate increases as the mixing speed increases until a certain point is reached where it starts to decrease.

Keywords: Carbon particles; Plastic spheres; Langmuir model; Deposition

1. Introduction

Deposition of carbon particles (as ink model) on plastic particles has been investigated in previous work as an alternative deinking technique [1,2]. It was shown that carbon particles could be collected from suspension by plastic particles with good removal ability [1]. The kinetics of the process was shown to be of Langmuir type [2]. The model presented [2] had the following dimensionless form:

$$n_\mathrm{d} = \frac{2(\lambda - 1)}{A(\lambda - 1) + B(\lambda + 1)} \tag{1a}$$

$$n = 1 - n_\mathrm{d} \tag{1b}$$

where

$$\lambda = \mathrm{e}^{k_1 B t} \tag{2}$$

$$A = \frac{1}{K} + \psi + 1 \tag{3}$$

$$B = \sqrt{(\psi - 1)^2 + \frac{2(\psi + 1)}{K} + \left(\frac{1}{K}\right)^2} \tag{4}$$

$$\psi = \frac{N_0}{N_{\mathrm{d\,max}}} \tag{5}$$

and K is the equilibrium constant given by the ratio

$$K = \frac{k_1}{k_2} \tag{6}$$

In the above equations, n is the ratio of the number of carbon particles in suspension at any time t to the initial value, n_d the ratio of the number of carbon particles deposited on the surface of the plastic particles at any time t to the initial value, k_1 the forward deposition coefficient, k_2 the detachment rate constant, N_0 the initial number of carbon particles per unit volume and $N_{\mathrm{d\,max}}$ is the maximum number of carbon particles the collector surface can accommodate. The three model parameters k_1, k_2 (or K) and ψ or $N_{\mathrm{d\,max}}$ could be determined from fitting the experimental deposition curves to the solution of the above equations [2]. van de Ven [3] showed that both physicochemical and hydrodynamic conditions had considerable effects on each of the two deposition coefficients (k_1 and k_2). For example, physico-

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Nomenclature

A	parameter given by Eq. (3)
B	parameter given by Eq. (4)
K	equilibrium constant
k_1	forward deposition constant
k_2	detachment rate constant
n	the ratio of the number of carbon particles in suspension at any time t to the initial value
n_{d}	the ratio of the number of carbon particles deposited on the surface of the plastic particles at any time t to the initial value
N_0	initial number of carbon particles in suspension
$N_{\mathrm{d\,max}}$	the maximum number of carbon particles the collector surface can accommodate

Greek letters

θ	equilibrium surface coverage
λ	parameter given by Eq. (2)
ψ	parameter given by Eq. (5)

chemical conditions can affect the bond strength (E) between the deposited particle and the collector surface and thus affecting the detachment rate (k_2) according to Eq. (5) in Ref. [2]. The hydrodynamic conditions affect the deposition efficiency, the collision rate constant and the pre-exponential constant in the expression of k_2 (see Ref. [2]).

For effective deinking, efforts should be directed towards increasing the removal efficiency by increasing equilibrium surface coverage ($\theta = \psi^* n_{\mathrm{d}}$) and decreasing the required deinking time (i.e. increasing deposition rate). Theoretically, these effects can be achieved by increasing the forward deposition coefficient and the equilibrium constant (i.e. with decreasing the backward detachment rate coefficient). In this paper, both the hydrodynamic and the physicochemical conditions were varied in order to study their effects on deposition kinetics. The hydrodynamic conditions were varied by changing the rotational speed in the stirred vessel (or the shear rate) while the physicochemical conditions were varied by changing the concentrations of the added chemicals ($CaCl_2$ and soap). The obtained experimental deposition curves were fitted to Langmuir model presented in [2]. The effects of the above conditions on model parameters are presented in this paper.

2. Experimental work

Sodium stearate solution was prepared according to the procedure followed by Young and Matijevic [4]. The pH of the solution was adjusted to a value of 7. To the above solution, a given amount of carbon black particles (BDH Chemicals of mean diameter = 25 μm) was added to have the required initial concentration of carbon particles of 0.25 g/l. Then low density polyethylene particles (QABCO of mean diameter = 3290 μm) were added such that the concentration is 5 g/l. The required amount of calcium chloride was also added. The total volume of suspension was 200 ml. The suspension was then stirred at the required rotational speed using a magnetic stirrer.

The effect of $CaCl_2$ concentration was studied by conducting experiments at $CaCl_2$ concentration of 0.05, 0.1, 0.3 and 0.5 g/l. Experiments with no calcium chloride were also performed. The effect of soap concentration was investigated by conducting experiments with soap concentrations equal to 0.9, 1.8, 3.6, and 9.0 mM. The effects of the rotational speed were examined by repeating the experiments at rotational speeds of 100, 300 and 500 rpm. The effect of each of the above parameters was studied by fixing the values of other parameters.

The rate of deposition of carbon particles on the plastic particles was followed by counting the number of carbon particles remaining in suspension as a function of time. This was done as follows: a sample of 2.5 ml from the suspension excluding plastic particles was taken at certain time intervals using a pipette. This was possible since the plastic particles are large in size. The sample was then transferred to a volumetric flask and diluted to 100 ml using distilled water (the dilution was made to minimize errors when counting the particles under the microscope). The diluted suspension was then filtered through Whatman #5 filter paper. The average pore diameter of this filter paper is 3 μm, much smaller than the size of the carbon particles. In this case, no carbon particles are lost during filtration. The filter paper was allowed to dry. It was then placed under the microscope (Olympus Optical, made in Japan) magnified 200 times. The images of the carbon particles were microphotographed at 15 different locations on the paper and then counted. The counted number of carbon particles at each time interval was divided by the initial number determined in the same way to obtain the dimensionless number of carbon particles in suspension (n).

3. Results and discussion

3.1. Effect of calcium chloride concentration

The effect of $CaCl_2$ on deposition rate was studied under rotational speed of 300 rpm, soap concentration of 1.8 mM, plastic concentration of 5 g/l and pH 7. Fig. 1 shows the effect of $CaCl_2$ concentration on the deposition rate when its concentration is below the stoichiometric amount necessary to react with the soap. The estimated parameters from fitting these results to the model are shown in Table 1. When no $CaCl_2$ is used, little deposition takes place. The reason for this is that stearate molecules deposit their hydrophobic ends on the carbon and the plastic particles since both particles are hydrophobic in nature. The hydrophilic ends are then directed towards water [5] rendering the particles negatively charged. Therefore, the repulsion between the

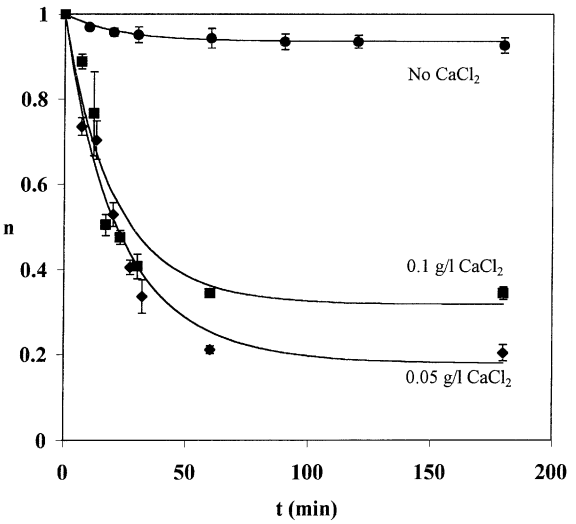

Fig. 1. Dimensionless number of carbon particles in suspension n versus time t for different $CaCl_2$ concentration below the stoichiometric amount necessary to react with the soap at pH = 7, mixing speed = 300 rpm, plastic concentration = 5 g/l, and soap concentration = 1.8 mM.

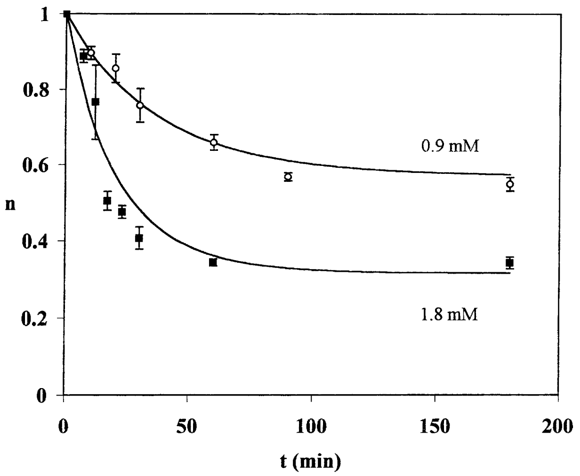

Fig. 2. Dimensionless number of carbon particles in suspension n versus time t for low soap concentrations at pH = 7, mixing speed = 300 rpm, $CaCl_2$ concentration of 0.1 g/l, plastic concentration = 5 g/l, and carbon concentration of 0.25 g/l.

particles overcomes the weak van der Waals attraction forces and hence no appreciable deposition takes place.

When $CaCl_2$ is added and its concentration (0.05 g/l suspension) is well below the stoichiometric ratio necessary to react with the sodium stearate the deposition rate was faster. The ratio of k_1 values in both cases is ∼13 indicating that the deposition rate becomes ∼13 times faster (see Table 1). It is expected that by further increasing $CaCl_2$ concentration more deposition will take place since Ca^{++} will reduce the electronegativity of the carbon and the plastic particles and hence decreasing the repulsion between them. In other words increasing the attraction forces. This was not the case. It was found that when $CaCl_2$ concentration was increased to 0.10 g/l (which is the stoichiometric amount necessary to react with the soap present), the number of carbon particles decreases in a similar fashion as the 0.05 g/l case. But the equilibrium value of n was higher (see Fig. 1). This means that the value of k_2 is higher. The reason for this is that as $CaCl_2$ concentration is increased, Ca^{++} reacts with stearate molecules forming insoluble calcium stearate. These particles precipitate on the surface of the carbon and the plastic particles. This enlarges the distance between the carbon and the plastic particles since the calcium stearate comes in between and thus weakening the attraction forces. Therefore, it becomes easy to detach the carbon from the plastic particles leading to a higher value of n at equilibrium or higher k_2 value. It also lowers the available sites for carbon deposition, which also decreases the deposition rate and results in a higher value of n at equilibrium.

Table 1
Model parameters estimated from fitting $CaCl_2$ deposition curves to Langmuir model

$CaCl_2$ (g/l)	k_1	k_2	K	ψ	$N_{d\,max}$
0	0.003	0.014	0.20	1.0	4.10×10^6
0.05	0.040	0.006	7.15	0.43	9.68×10^6
0.1	0.036	0.012	3.05	0.43	9.60×10^6

3.2. *Effect of soap concentration*

Effect of soap concentration on the deposition kinetic is shown in Figs. 2 and 3. The experiments were done at a fixed $CaCl_2$ concentration (0.1 g/l suspension). It can be seen that the fastest deposition rate occurs when the soap concentration equals 1.8 mM which is the amount necessary to react with the soap present. Fig. 3 confirms this observation. Moreover, the deposition rate appears to be faster for soap concentration below 1.8 mM (excess Ca^{++}) compared to the concentrations of soap above 1.8 mM (excess stearate

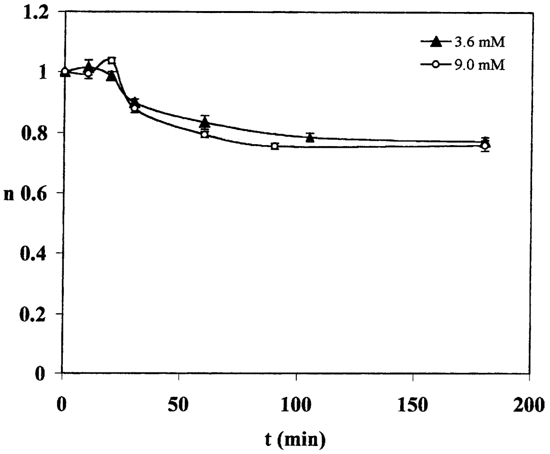

Fig. 3. Dimensionless number of carbon particles in suspension versus time for high soap concentrations at pH = 7, mixing speed = 300 rpm, $CaCl_2$ concentration of 0.1 g/l, and plastic concentration = 5 g/l.

Table 2
Model parameters estimated from fitting various soap concentration deposition curves to Langmuir model

Soap concentration (mM)	k_1	k_2	K	ψ	$N_{\mathrm{d\,max}}$
0.9	0.012	0.013	0.923	0.43	9.6×10^6
1.8	0.036	0.012	3.055	0.43	9.6×10^6

Table 3
Model parameters estimated from fitting mixing speed deposition curves to Langmuir model

Mixing speed (rpm)	k_1	k_2	K	ψ	$N_{\mathrm{d\,max}}$
100	0.007	0.010	0.704	0.479	8.63×10^6
300	0.036	0.012	3.055	0.430	9.60×10^6
500	0.009	0.012	0.740	0.486	2.13×10^6

molecules). For the cases where the soap concentration is 3.6 and 9.0 mM, no appreciable difference in deposition rate was noticed (see Fig. 2).

For the case where the soap concentration equals 1.8 mM the stearate molecules react with Ca^{++} reducing the electrical repulsion between the particles resulting in a high affinity of the carbon to the plastic and hence in a fast deposition rate compared to the other cases. Decreasing the soap concentration below 1.8 mM (excess Ca^{++} is present) results in a decrease in the deposition rate (see Fig. 2). The particles in this case are less hydrophobic and its affinity to the plastic is also less. In other words, if we think of the calcium stearate particles as the bonds that bridge the carbon to the plastic (the case when Ca^{++} is high [6,7]), then lowering the soap concentration means that the bonds between these particles become weaker. In this case, detachment of the carbon particles is easier. The experimental results for the above cases follow Langmuir kinetics. The solid curves in Fig. 2 represents the fitting of these experimental results to the model. The estimated parameters are tabulated in Table 2.

For the cases where the soap concentration is above 1.8 mM, excess soap molecules are presented in the suspension. These molecules deposit their hydrophobic end on the carbon and the plastic particles leaving them negatively charged. Hence a net repulsion exists between the carbon and the plastic particles. This results in a decrease in the deposition rates and makes their values similar (see Fig. 3).

3.3. Effect of rotational speed on deposition rate

Fig. 4 shows the effect of rotational speed on deposition rate. The experiments were done with the following conditions: soap concentration = 1.8 mM, calcium chloride concentration = 0.10 g/l, plastic concentration = 5 g/l and pH = 7. The estimated parameters from fitting these results to the model are shown in Table 3. The forward deposition coefficient and the backward detachment coefficient are plotted in Fig. 5. It can be seen that as the rotational speed increases from 100 to 300 rpm, the forward deposition rate increases. Further increase in the rotational speed to 500 rpm decreases the deposition rate. The reason for this can be explained as follows. As the rotational speed increases, the number of collisions between the carbon and the plastic particles increases according to [8,9]. This leads to a faster deposition rate. However, at high shear rate the deposition efficiency, which is a measure of the successful collisions to the total collisions, is inversely proportional to the shear rate [10,11]. These two opposing situations explain the behavior of the curves in Figs. 4 and 5. It can be also seen from Fig. 5 that increasing the rotational speed will increase the backward detachment rate. This proves that the forward deposition rate is proportional to the collision efficiency, while the backward detachment rate depends on shear rate (see Eqs. (2) and (5) of Ref. [1]).

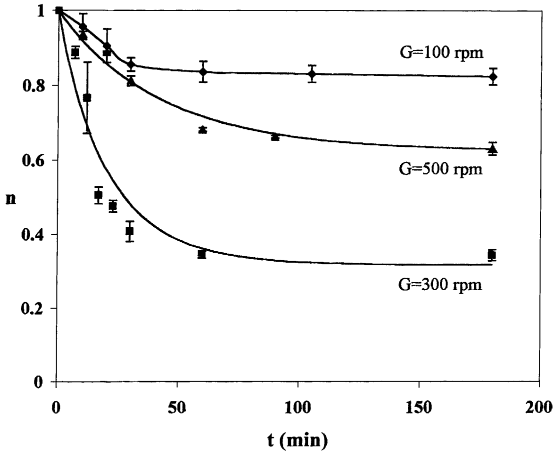

Fig. 4. Dimensionless number of carbon particles in suspension n versus time t for different mixing speeds at PpH = 7, $CaCl_2$ concentration = 0.1 g/l, carbon concentration = 0.25 g/l, plastic concentration = 5 g/l,, and soap concentration = 1.8 nM.

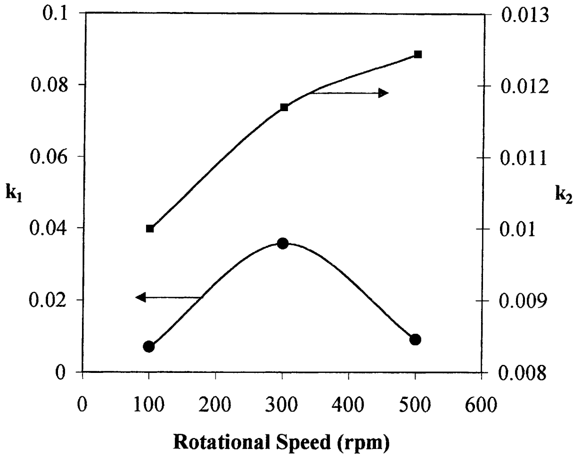

Fig. 5. The forward deposition coefficient k_1 and the backward detachment coefficient k_2 as a function of mixing speed.

4. Conclusions

Deposition using plastic particles is an alternative method for deinking. Deposition of carbon particles onto plastic particles has a qualitative behavior similar to other deposition systems investigated previously. The kinetics of carbon deposition on the surface of plastic particles follows Langmuir kinetics.

Calcium ions play an important role in the deposition of carbon particles on plastic particles. The formation of calcium stearate particles bridges the carbon to the plastic particles.

The best concentration of soap for deposition is the stoichiometric amount necessary to react with the calcium chloride. Below this value, particles are less hydrophobic and its affinity to plastic particles is less. At concentrations above the stoichiometric amount the particles are negatively charged and lower deposition rate results. A further increase in the soap concentration has no effect on the deposition rate.

Both the deposition rate and the number of carbon particles at equilibrium increase as the mixing speed increases until a maximum value is reached where they start to decrease. The forward deposition rate constant goes through a maximum as the mixing speed increases while the detachment rate constant is directly proportional to it.

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