

*Dedicated to Professor Emil Cordoş
on the occasion of his 80th anniversary*

EVALUATION OF MASS TRANSFER PARAMETERS FOR UREA DISSOLUTION IN FIXED-BED WITH DOWNWARD FLOW OF WATER

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ABSTRACT. The current study aimed to evaluate the mass transfer parameters for the dissolution of spherical urea particles in fixed bed with downward flow of water. The impact of several operating parameters (particle size, height of the bed, liquid flow rate) on the key mass transfer parameters was investigated in isothermal conditions and atmospheric pressure. It was found that the mass transfer coefficient and urea dissolution degree increases by flow rate increase and decreases with the increase of particle size and bed height. The experimental values of the mass transfer coefficients were in good agreement with the ones found in the literature and the ones predicted by the Cussler equation.

Keywords: *urea dissolution, mass transfer coefficient, dissolution degree, packed bed, downward flow*

INTRODUCTION

The study and understanding of fundamental aspects of two phase solid-liquid mass transfer is a key issue in the design of catalytic and non-catalytic chemical and biochemical reactors with application in wastewater treatment, liquid–solid circulating fluidized beds, treatment of solid–liquid mixtures [1-3]. Among different types of industries, the dissolution and extraction of valuable minerals also requires the identification of key mass transfer parameters [4]. Fixed and fluidized bed reactors are one of the

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most important equipments of the chemical industry having a wide range of industrial and environmental applications [5, 6]. Depending on the structure of the bed of particles, these reactors offer a potential solution for process intensification by increasing the surface contact area between the two phases [7]. In addition to the increase of the heterogeneous reaction rate the increase of surface contact area per unit volume also improves the heat transfer parameters and lowers the capital costs involved in the acquisition of different process equipment [5, 8]. According to the literature, the most common approaches for the study of mass transfer in solid - liquid systems using fixed and/or fluidized beds are: dissolution, adsorption, ion exchange, electrochemical methods, using columns with short or long bed of active particles [9, 10]. In many situations the active particles consist of spherical or cylindrical cores coated with a thin layer of the melted active substance [11, 12]. The most important techniques used in the literature for the evaluation of key mass transfer parameters involve fixed and fluidized bed dissolution, rotating disc method and plug flow systems [13]. The dissolution techniques are applied in isothermal and isobaric conditions, mainly at atmospheric pressure and ambient temperature with upward or downward flow of the fluid. According to the literature distilled water is the most common solvent but if the technology requires aqueous solution of the active substance or other impurities may be also used as dissolution medium [14]. Heterogeneous mass transfer is also of great importance in the case of nutrient uptake and assimilation in plants. It is necessary to understand and control the dissolution of different fertilizers in order to achieve efficient plant growth and high production yields [15].

Considering the industrial and agriculture importance of urea dissolution, this paper studies the dissolution of solid urea in fixed bed with downward flow of the dissolution medium. The study revealed the dependence of key mass transfer parameters on bed height, particles diameter and solvent flow rate.

RESULTS AND DISCUSSION

The identification of the mean mass transfer coefficients at different experimental conditions was based on the following assumptions:

- During the dissolution urea particles were considered perfectly spherical of the same diameter and density.
- The initial number of particles remains constant and the change in the particle size is uniform in the bed.
- The dissolution rate is the same for all the particles and changes similarly in time for all of them.

Based on the above assumptions, the *number of particles* (N_p) in the bed was determined from the amount of material introduced into the column:

$$N_p = \frac{6 \cdot m_o}{\pi \cdot \rho_p \cdot d_o^3} \quad (1)$$

where: m_o - amount of urea introduced into the column, (kg); ρ_p - urea density, ($\text{kg}\cdot\text{m}^{-3}$); d_o - initial diameter of the urea particles, (m).

The amount of non-dissolved urea ($m_{col,i}$) can be determined by subtracting the quantity of dissolved urea over a period of time from the initial amount. As a result the diameter of the particle (d_i) may be determined from the following equation:

$$d_i = \left(\frac{6 \cdot m_{col,i}}{\pi \cdot \rho_p \cdot N_p} \right)^{1/3} \quad (2)$$

The mass transfer area is variable during the dissolution and can be calculated from the number and diameter of the particles found in the column:

$$A_i = \pi \cdot N_p \cdot \bar{d}_i^2 \quad (3)$$

where: A_i - the particles surface, (m^2) and \bar{d}_i - the average particle diameter for the period of time for which the contact surface area is calculated, (m).

The mass transfer coefficient can be determined from the experimental results using the equation:

$$k = \frac{\Delta m}{A_i \cdot \Delta t \cdot \Delta C_{med}} \quad (4)$$

where: k - mean mass transfer coefficient for period Δt , ($\text{m}\cdot\text{s}^{-1}$); Δm - amount of dissolved urea over a period of time Δt , (kg); Δt - dissolution time period, (s) and ΔC_{med} - log mean driving force, ($\text{kg}\cdot\text{m}^{-3}$).

According to the literature the driving force can be calculated as the difference between the saturation concentration and the concentration of urea at the exit of the column or by the log mean driving force defined by eq. (5). In particular when the solute concentration at the entrance is equal to zero both methods give comparable values for the driving force. However, the driving force for urea dissolution was determined by eq. (5), considering that even in this particular situation several studies recommend the use of the log mean driving force.

$$\Delta C_{med} = \frac{(C^* - C_i) - (C^* - C_f)}{\ln \frac{C^* - C_i}{C^* - C_f}} \quad (5)$$

where: C^* - saturation concentration of urea, ($\text{kg}\cdot\text{m}^{-3}$); C_i - initial concentration of urea, ($\text{kg}\cdot\text{m}^{-3}$) and C_f - final concentration of urea, ($\text{kg}\cdot\text{m}^{-3}$).

The results presented in Fig. 1 show that the mean mass transfer coefficients, calculated for the dissolution of urea particles with diameter of 1.25 mm, are almost constant in time but are significantly influenced by bed height and flow rate variations. It can be seen that flow rate increase has a positive impact on the mean mass transfer coefficients, which is related to the intensification of the process due to the greater liquid velocity in the intergranular spaces. In contrast, the increase of the particle bed height reduces the mean mass transfer coefficients due to the fact that the mean driving force increases as well as the values of urea concentration in the effluent.

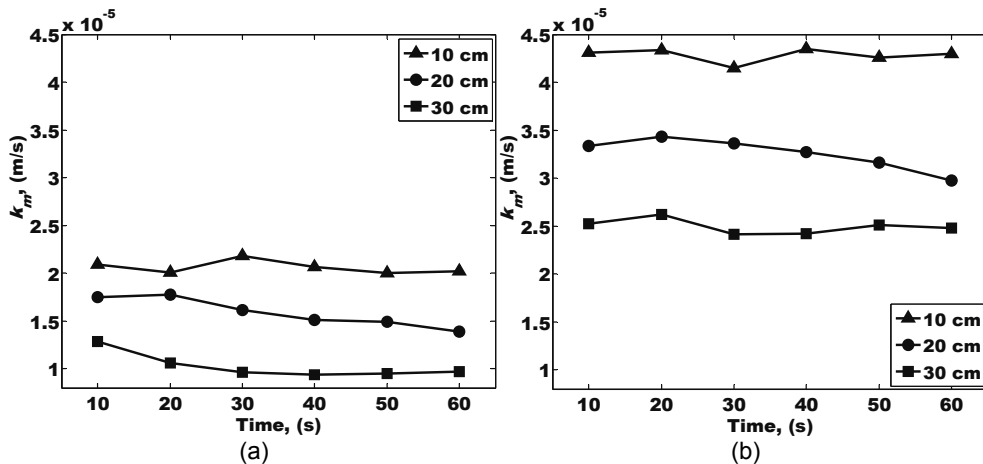


Figure 1. Mass transfer coefficient vs. time at different bed heights using particles with diameter of 1.25 mm and flow rates of (a) 3.5 L/h and (b) 7 L/h.

Increasing the diameter of the urea particles from 1.25 mm to 2 mm leads to the decrease of mass transfer coefficients regardless the applied flow rate or particle bed height. Similarly, at constant bed height, flow rate increase from 3.5 L/h to 7 L/h almost doubles the mean mass transfer coefficient, while bed height increase from 10 cm to 30 cm halves it regardless the flow rate (Fig. 2). It is also important to note that the results found in the current study regarding the dependence of the mean mass

transfer coefficients on flow rate, particle size and bed height are in good agreement with the ones found in the literature [7].

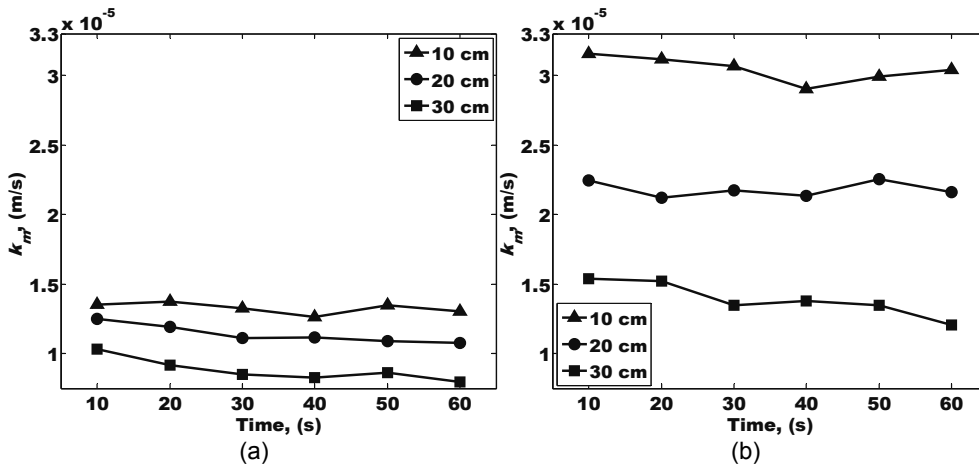


Figure 2. Mass transfer coefficient vs. time at different bed heights using particles with diameter of 2 mm and flow rates of (a) 3.5 L/h and (b) 7 L/h.

The experimental mean mass transfer coefficients were compared with the theoretical ones given by Cussler's equation:

$$k = 1.17 \cdot v_0 \cdot \left(\frac{d \cdot v_0}{\nu} \right)^{-0.42} \cdot \left(\frac{D}{\nu} \right)^{0.66} \quad (6)$$

where: v_0 - fluid velocity in the column, ($\text{m} \cdot \text{s}^{-1}$); d - urea particle diameter, (m); ν - kinematic viscosity of the solution, ($\text{m}^2 \cdot \text{s}^{-1}$) and D - diffusion coefficient of urea in water, ($\text{m}^2 \cdot \text{s}^{-1}$).

For instance, as it's shown in Fig. 3, the evolution in time of the experimental and theoretical mass transfer coefficients at the same flow rate of 7 L/h. It can be noticed that in the first part of the experiments the measured and predicted mass transfer coefficients values are close to each other, while in the final stage of the experiment the difference between the theoretical and experimental values increases significantly. This can be accounted to the fact that particle characteristics become more diverse as the dissolution process advances in time, especially at low particle diameters. For this reason, the discrepancies between the measured and predicted mass transfer coefficient values are even greater for the experiments with 1.25 mm particle diameter.

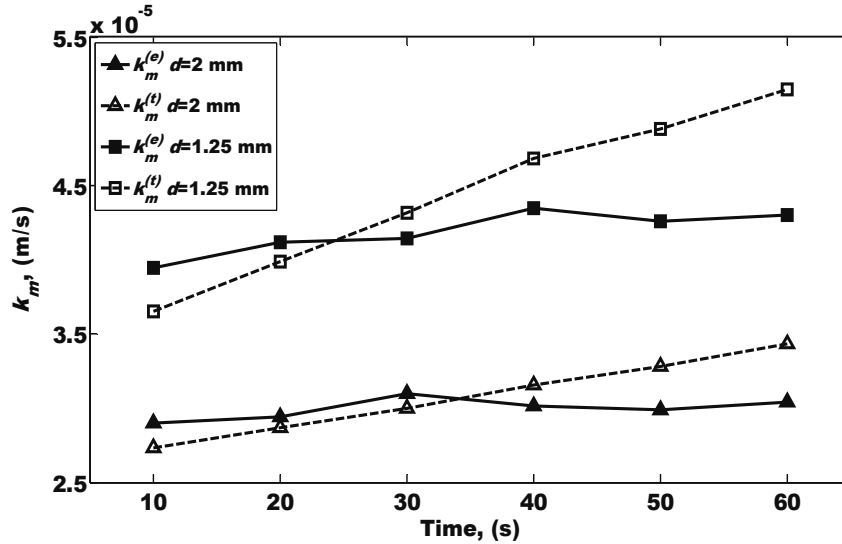


Figure 3. Experimental ($k_m^{(e)}$) and theoretical ($k_m^{(t)}$) mass transfer coefficients vs. time at the flow rate of 7 L/h using particles with diameter of 1.25 mm and 2 mm.

In order to evaluate the efficiency of urea dissolution, the mean dissolution degree of urea was determined for all the experimental conditions. According to eq. (7), the mean dissolution degree of urea (η_i) over a period of time (Δt_i) was defined as the ratio between the amount of dissolved urea (Δm_i) and the amount of urea introduced into the column at the beginning of the experiment (m_o):

$$\eta_i = 100 \cdot \left(\frac{\Delta m_i}{m_o} \right) \quad (7)$$

Fig. 4 shows that the mean dissolution degree of urea for a constant particle diameter of 1.25 mm increases in time regardless the applied flow rate or initial bed height. It can be also observed that the decrease of the bed height of particles for both flow rates leads to a more rapid increase of the mean dissolution degree. However, it seems like at the lowest flow rate the mean dissolution degree is more sensitive to bed height variations than at highest flow rate.

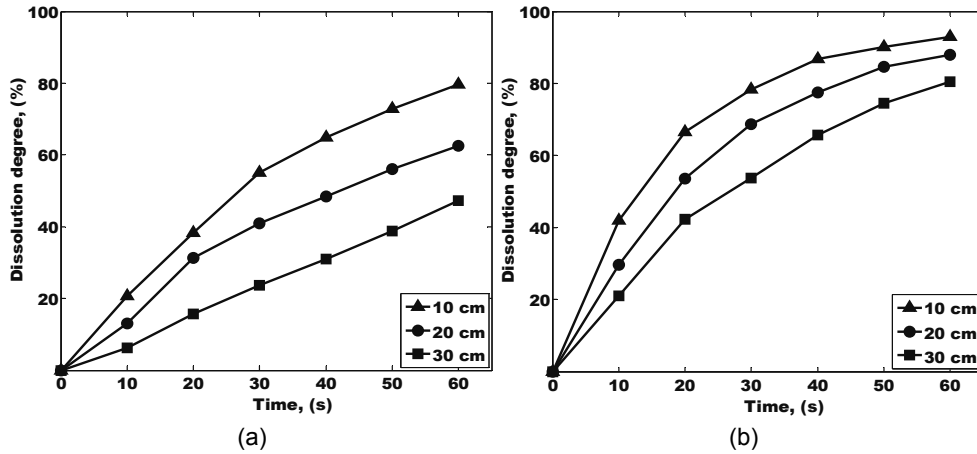


Figure 4. Dissolution degree vs. time at different bed heights; particles diameter of 1.25 mm and flow rates of (a) 3.5 L/h and (b) 7 L/h.

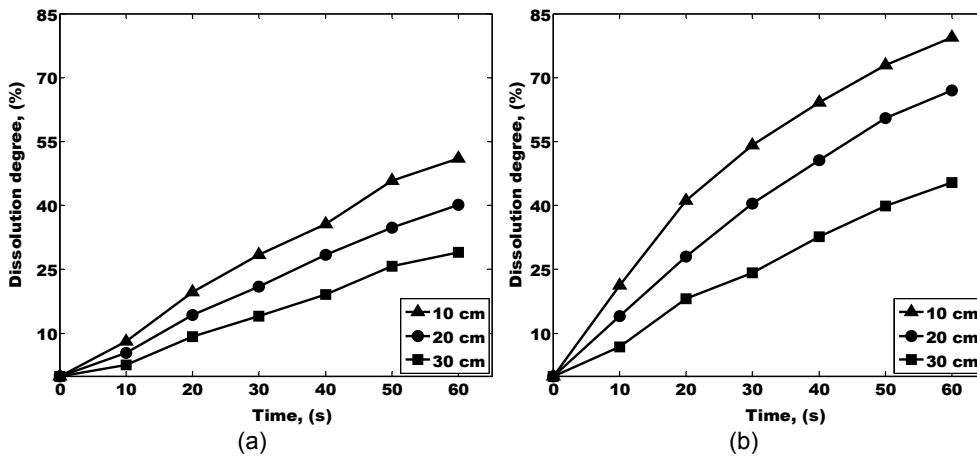


Figure 5. Dissolution degree vs. time at different bed heights using particles with diameter of 2 mm and flow rates of (a) 3.5 L/h and (b) 7 L/h.

As can be seen from Fig. 5, the mean dissolution degree follows similar tendency at the dissolution of particles with an initial diameter of 2 mm. Still, in the same experimental conditions the mean dissolution degree values are smaller for the particles with 2 mm than for the ones with 1.25 mm. This can be accounted to the fact that the urea particles with 1.25 mm diameter offer a larger solid-liquid contact surface area at the

same bed height than the ones with a diameter of 2 mm. For the same reason, the mean dissolution degree values differ more between the highest and lowest bed heights for the experiments with particle diameter of 2 mm than for the ones with 1.25 mm diameter. This difference is the most obvious at the flow rate of 7 L/h where for the experiments with particles of 2 mm diameter the mean dissolution degree increases with 75 % between the bed heights of 10 cm and 30 cm, while for the experiments with particles of 1.25 mm diameter it increases with only 15 % for the same variation of bed height.

CONCLUSIONS

The key mass transfer parameters were identified for the dissolution of spherical urea particles in fixed bed with downward flow of water. The experimental results indicate that the increase of flow rate increases the mean mass transfer coefficients as well as the dissolution degree of urea regardless the applied operating conditions. It was also found that the increase of particle diameter and height of the fixed bed have a negative impact on the key mass transfer parameters. The study also revealed that mean mass transfer coefficients can be predicted by the Cussler's equation considering the good agreement between the experimental and theoretical values given by Cussler's equation.

As an overall conclusion it can be stated that the dissolution of spherical urea particles occurs the most efficiently by using the highest flow rate, lowest bed height and particle diameter.

EXPERIMENTAL SECTION

The experiments were performed at room temperature and atmospheric pressure using a cylindrical glass column with an internal diameter of 2.1 cm and a height of 50 cm. The granular material was sustained by the perforated plate found at the bottom of the column.

The dissolution study was conducted in a fixed bed at different bed heights (10, 20, 30 cm) using two urea fractions with particles of 1.25 and 2.00 mm diameter.

Distilled water was used as the dissolution medium and a centrifugal pump ensured the necessary flow rates (3.5 and 7.0 L/h) through the column (Fig. 6).

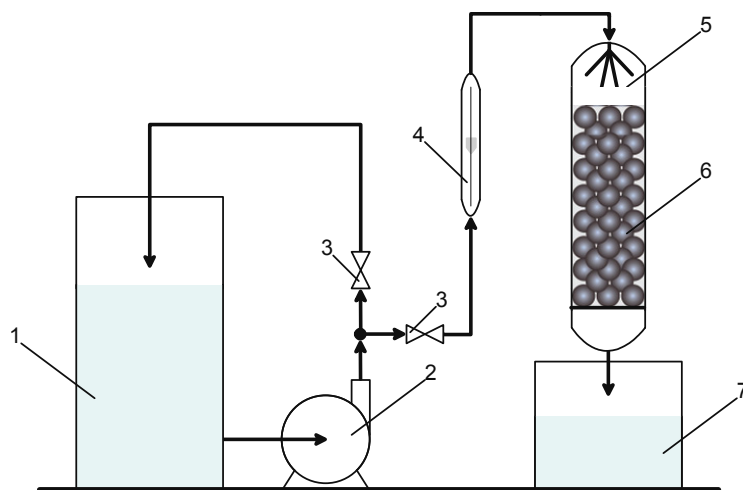


Figure 6. The experimental setup: 1 - water tank; 2 - pump; 3 - valve; 4 - rotameter; 5 - dissolution column; 6 - granular urea; 7 - solution tank.

At different time intervals, the solution exiting the column was sampled in order to determine the concentration of urea and the amount of dissolved urea.

Sample concentration (C) was determined based on a calibration curve (Fig. 7) using refractive index (n) measurements:

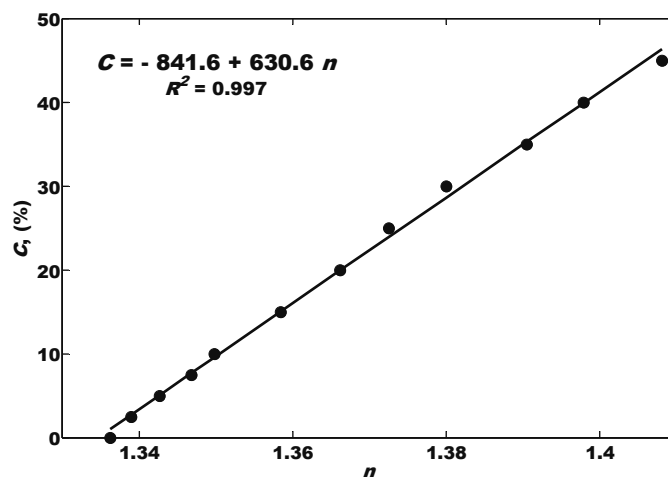


Figure 7. The calibration curve used for measurements

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