

## Supporting Information

### Developing and verifying a quantitative dissolution model for metal-bearing nanoparticles in aqueous media

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## Supporting Information 1

### 1.1. Data collection

Data used for the model was collected from the Web of Science (WOS) for the period 2010-2020 (cutoff date: March 30, 2020). Studies included in the final search were restricted by two conditions: a) the research topic needed to contain “dissolution\*” or “\*ions” or “\*fate” or “\*transformation”; and b) either the title or the abstract had to contain “nano” or “quantum”. Besides, the reference lists of the results retrieved were checked to find related investigations (so-called snow ball method). In total 504 studies were identified from the retrieved results and further refined according to the following criteria: i) the experiment was conducted in aqueous medium, ii) the shape of the NPs was spherical, and iii) the size, initial concentration and dissolution profile of the NPs were clearly reported. Based on the above criteria, 17 useful papers were retained and studied in detail.

To parametrize the dissolution model, it was needed to obtain the raw data of the dissolution experiment in order to reproduce the dissolution curve. From the papers selected, the ion concentration at each time point was derived from the published graphs by using "Web Plot Digitizer" (version 4.2). It is to be noted that often the initial ion concentration deviates from zero, amongst others due to unintended exposure to oxygen as in case of Ag NPs<sup>1</sup> or due to ion release during the preparation of the NP suspensions before the very first sampling time. The individual data points on release kinetics thus contain experimental uncertainty and uncertainty in the timing of the data points. The level out these uncertainties as much as possible, we derived as a first step in our model approach a simple model for quantifying overall ion release in the initial stages of the dissolution process.

### 1.2. Step 1 (data preprocessing)

Ion release of metal-bearing NPs is assumed to follow pseudo-first order kinetics, the rate constant of which is equal to the slope of the dissolution curve at time  $t = 0$  (equation 1):

$$(1) C_{NP(t)} = C_{NP(0)} e^{-W_{ion} t},$$

which can be transformed into:

$$(2) \ln(C_{NP(t)}/C_{NP(0)}) = -W_{ion} t,$$

In these equations,  $C_{NP(t)}$  and  $C_{NP(0)}$  represent the particle concentrations ( $\text{mg L}^{-1}$ ) at times  $t$  and 0 respectively, and  $W_{ion}$  represents the slope of the dissolution curve with a unit of  $\text{h}^{-1}$ . The total metal concentration in the NPs suspensions always stays the same during the dissolution. So conservation of mass implies:

$$(3) C_{NP(t_0)} + C_{ion(t_0)} = C_{NP(t_1)} + C_{ion(t_1)}, \text{ at any 2 time points } t_0 \text{ and } t_1.$$

Also from equation 1 we find that:

$$(4) C_{NP}(t_0) = C_{NP}(0) e^{-W_{ion}t_0}.$$

Then substituting equations 1 and 4 into equation 3 gives:

$$(5) C_{NP}(0) e^{-W_{ion}t} + C_{ion}(t) = C_{NP}(0) e^{-W_{ion}t_0} + C_{ion}(t_0).$$

Thus, finally we find that

$$(6) C_{ion}(t) - C_{ion}(t_0) = C_{NP}(0) [e^{-W_{ion}t_0} - e^{-W_{ion}t}].$$

Next, we assume that  $W_{ion} t_0$  and  $W_{ion} t$  are both “small”, hence lie close to zero. Then, we can approximate the exponential by a linear function by using a Taylor expansion after which we obtain that:

$$(7) C_{ion}(t) - C_{ion}(t_0) = C_{NP}(0) (t - t_0) W_{ion}.$$

To determine the slope  $W_{ion}$ , the first few data points were used at the initial dissolution stage when a linear relationship could still be plotted for ion concentration and time. Outliers should be identified if:

- Constant ion concentration is observed at two or more than two consecutive time points. In that case only the first data point is used;
- Lower ion concentration occurs at a later time point from the curve.

After obtaining the initial ion concentration for the dissolution kinetics, we extracted the concentration of ions in the suspension when it reached equilibrium or a steady state. This information was derived from the original curve presented in the paper. The steady state concentration was pragmatically defined as the concentration that did not change by more than 10 % during three consecutive data points. The first of these time points was defined as the time needed to reach steady state. In the system where ion concentration continues to increase during the measurements, the steady state concentration is not determined in the experiment and this is marked as “-” in the tables.

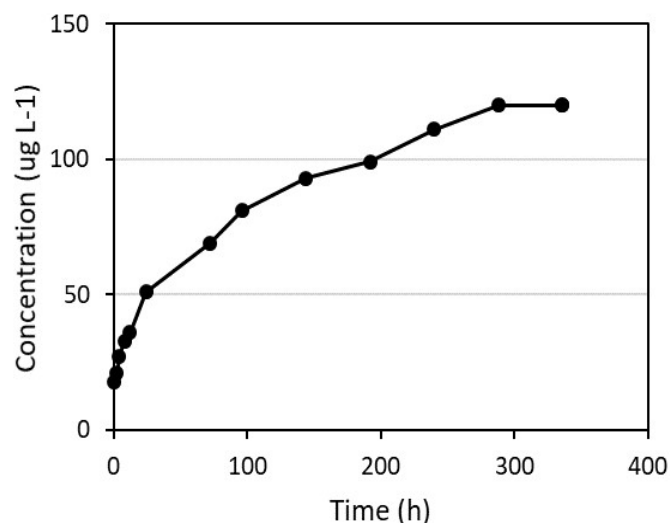
To illustrate the calculation of the initial stage of dissolution, we use the data reported in the study of Zhang <sup>1</sup> as an example. Figure 1 displays the time-dependent increase of the concentration of silver ions in the exposure medium, following suspension of Ag NPs with a particle size of 20 nm and an initial particle concentration of 300  $\mu\text{g L}^{-1}$ . The data points related

to the lowest exposure times (from 0 to 336 h) were selected in the first step. The data of interest reflected the initial dissolution kinetics - defined as the slope of the dissolution curve at  $t = 0$ . Obviously, the slope of the dissolution curve decreased upon reaching apparent equilibrium after 336 h of exposure. In this case,  $C_{NP}(0)$  is  $300 \mu\text{g L}^{-1}$  and the initial two data points (2,  $C_{ion}(2)$ ) and (8,  $C_{ion}(8)$ ) were used to calculate the slope  $W_{ion}$  and using equation (7) we obtain:

$$C_{ion}(8) - C_{ion}(2) = C_{NP}(0) (8 - 2) W_{ion},$$

$$W_{ion} = 0.0067 \text{ h}^{-1}.$$

Subsequently, we can calculate the ion concentration  $C_{ion}(t)$  at any time point by using expression (7), as long as  $W_{ion} t$  is small. For instance, we determine the  $C_{ion}(0) = 17 \mu\text{g L}^{-1}$  and  $C_{ion}(10) = 37 \mu\text{g L}^{-1}$ .



**Figure S1.** The dissolution curve of spherical Ag NPs of size 20 nm as determined during 336 hours of exposure at a concentration of  $300 \mu\text{g L}^{-1}$ .

## Supporting Information 2

**Table S1.** Impact of nanoparticle radius on dissolution rate constants.

| NPs | Radius<br>(nm) | $k$<br>(ng cm <sup>-2</sup> h <sup>-1</sup> ) | Reference |
|-----|----------------|---|-----------|
| Ag  | 2.4            | 3.8-24.6                                      | 2         |
| Ag  | 10-40          | 5.9-35.6                                      | 1         |
| Ag  | 19.5           | 0.02-1.7                                      | 3         |
| Ag  | 25             | 0.1-3.6                                       | 4         |
| Ag  | 15-30          | 1.75-8.5                                      | 5         |
| Cu  | 12.5-250       | 0.04-0.5                                      | 6         |
| Cu  | 12.5-250       | 11.6-341.7                                    | 7         |
| Cu  | 25             | 81  | 8         |
| Cu  | 25-250         | 3.1-71.6                                      | 9         |
| CuO | 20             | 32.4-74.4                                     | 10        |
| ZnO | 2              | 0.04-0.7                                      | 11        |
| ZnO | 20             | 0.04-0.1                                      | 12        |
| ZnO | 18-43          | 1.7-1.8                                       | 9         |

$k$  = dissolution rate constant (ng cm<sup>-2</sup> h<sup>-1</sup>).

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