# NMR relaxometry for adsorption studies: proof of concept with copper adsorption on activated alumina

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*The measurement of the transverse relaxation rate is used to follow "live" the adsorption of $Cu^{2+}$ ions on activated alumina using only 350 µl of solution and 45 mg of adsorbent. The longitudinal relaxation of the $Cu^{2+}$ containing adsorbent is also studied.*

## 1. Pollution of water by heavy metals

- The presence of heavy metals in water is a major health concern[1,2],
- Some of those metals are paramagnetic, like $Cu^{2+}$, $Ni^{2+}$, $Cr^{3+}$...
- MRI was already used to monitor the migration of paramagnetic ions in different matrixes[3,4],
- The idea is to use NMR relaxometry to follow the adsorption of magnetic ions on $Al_2O_3$,
- Relaxometry is cheap, can be miniaturized and is rather easy to implement.

## 2. Adsorption kinetics study using $T_2$ relaxometry

- Principle of the experiment[5] illustrated on figure 1: adsorption directly in the NMR tube,
- From the value of $T_2$ at 0.47 T, the remaining content of $Cu^{2+}$ in the solution is determined,
- Then the amount of copper on alumina is calculated with:

$$M(Cu) = V_{sample}\ A_{Cu}\left([Cu]_{ini} - \frac{1/T_2 - 1/T_2^{water}}{r_2}\right) \quad (1)$$

- The evolution with time of $q$ (amount of $Cu^{2+}$ per mg of $Al_2O_3$) allows to obtain the kinetics curve (figure 2) which follows a second-order model (Eq. 2). $q_e$ is the equilibrium content of copper on $Al_2O_3$ and k is the rate constant.

$$\frac{t}{q_t} = \frac{1}{k\,q_e^{\,2}} + \frac{t}{q_e} \quad (2)$$

***Figure 2:*** *kinetics of the adsorption of $Cu^{2+}$ on alumina. 350 µl of 10 mM $Cu^{2+}$ solution and 45 mg of alumina. T = 20°C and pH = 4. Line is a fitting by a second-order adsorption model.*

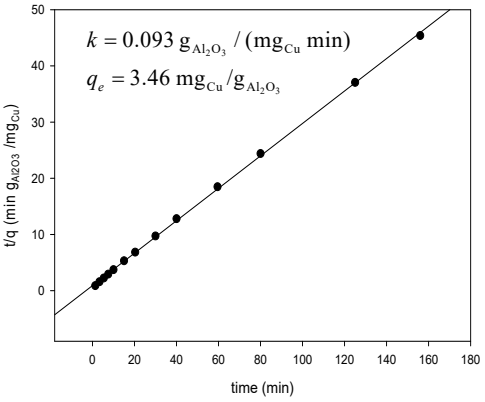
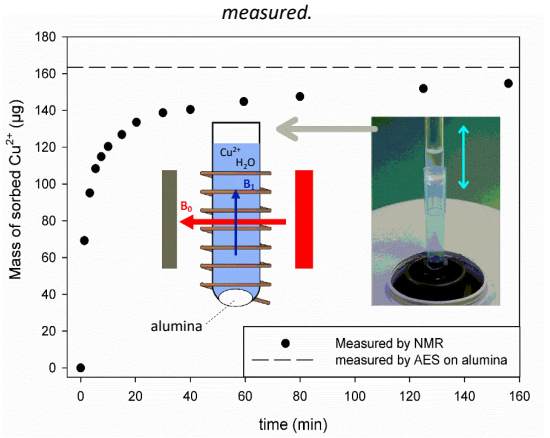
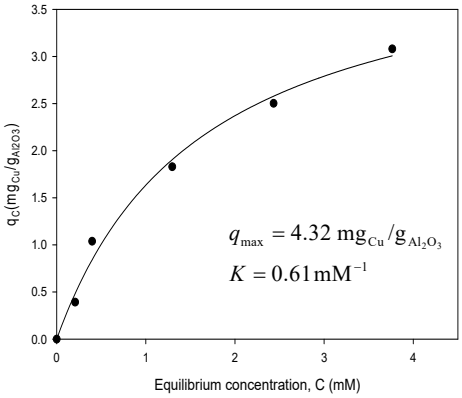



***Figure 1:*** *sketch of an experiment. The sorbent and the solution are placed in a 7.5 mm NMR tube which is shaken on a vortex mixer. At different time intervals, $T_2$ of the solution is measured.*




## 3. Adsorption isotherm and equilibrium constant

- Preparation of 5 NMR tubes with 350 µl of different [$Cu^{2+}$] solutions and 45 mg of sorbent,
- Shaking during 2 hours,
- Measurement of $T_2$ with a CPMG sequence for all the tubes,
- Calculation of $q_c$, the amount of copper adsorbed on $Al_2O_3$ with (1),
- Fitting of the isotherm with the Langmuir adsorption model (3):




$$q_C = q_{max}\frac{K \cdot C}{1 + K \cdot C} \quad (3)$$

***Figure 3:*** *adsorption isotherm for $Cu^{2+}$ on $Al_2O_3$ at T = 20°C and pH 4. Line is a fitting by the Langmuir model.*

## 4. Relaxation of copper-containing alumina

- Preparation of copper-containing $Al_2O_3$ with usual batch experiments,
- Drying and preparation of an NMR tube containing 0.29 g of dry powder and 200 µl of water,
- Recording of the saturation recovery curve for $Al_2O_3$ samples containing different amounts of copper (figure 4a),
- Correlation of the signal at 6.8 ms with copper content (figure 4b).

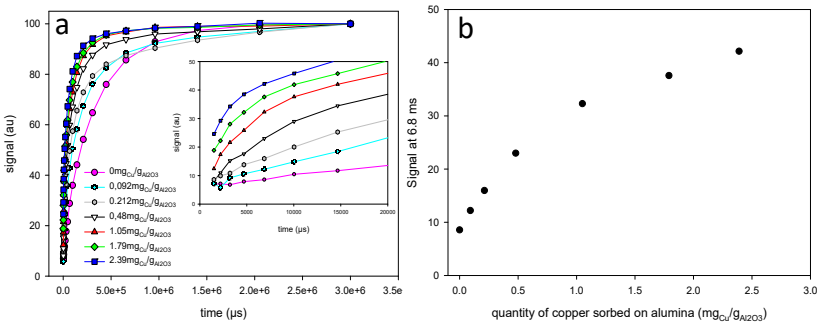



***Figure 4:*** *(a) longitudinal relaxation of alumina containing different amounts of copper during a saturation-reparation curve. (b) influence of the copper content on the signal at 6.8 ms.*

## 5. Perspectives

- Same experiments with other paramagnetic ions ($Ni^{2+}$, $Cr^{3+}$...)
- Test new adsorbents (ion exchanging resins, activated carbon...)
- Online measurements during a column experiment, inside the magnet of a low resolution NMR relaxometer.

## References

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