Benchtop NMR relaxometry for the follow-up of Cr(III) and Mn(II) removal by ion exchange resin.

M. Bernardi[1,a], A-L Hantson[2] and Y. Gossuin[1]

[1] Biomedical Physics Department, UMONS
[2] Chemical and Biomedical Engineering Department, UMONS
[a]corresponding author: marie.bernardi@umons.ac.be

Context

Heavy metals ions such as Mn(II) and Cr(III) are known to be toxic and must be removed from wastewater [1]. These ions also have paramagnetic properties which allowed the use of Nuclear Magnetic Resonance (NMR) relaxometry to monitor their removal from water by a strong cation exchange resin [2-3]. In this research, kinetic and equilibrium isotherm experiments were performed.

Model

From the value of T_1 or T_2 measured, the amount of heavy metal ions adsorbed on the resin (q) can be determined with:

$$q = \frac{VA}{m}\left[C_0 - \frac{\left(\frac{1}{T_{water}} - \frac{1}{T}\right)}{r_i}\right] \quad (1)$$

With V, the volume of solution; A, the atomic weight; C_0, the initial ion concentration; r_i (i=1,2), the relaxivity and m, the mass of resin.

The kinetic of adsorption can be described by the Pseudo-First Order kinetic model:

$$q(t) = q_{e,F}\left(1 - e_1^{-k_1 t}\right) \quad (2)$$

Or by the Pseudo-Second Order model:

$$q(t) = \frac{k_2 q_{e,S}^2\, t}{1 + k_2 q_{e,S} t} \quad (3)$$

where $q_{e,F}$ and $q_{e,S}$ are the amount of metal in the resin at equilibrium obtained by the Pseudo-First order and Pseudo-Second order model respectively; k_1 and k_2 are the kinetic constants.

The Langmuir Isotherm can predict the maximum adsorption capacity (q_{max}) of a resin for different metal species:

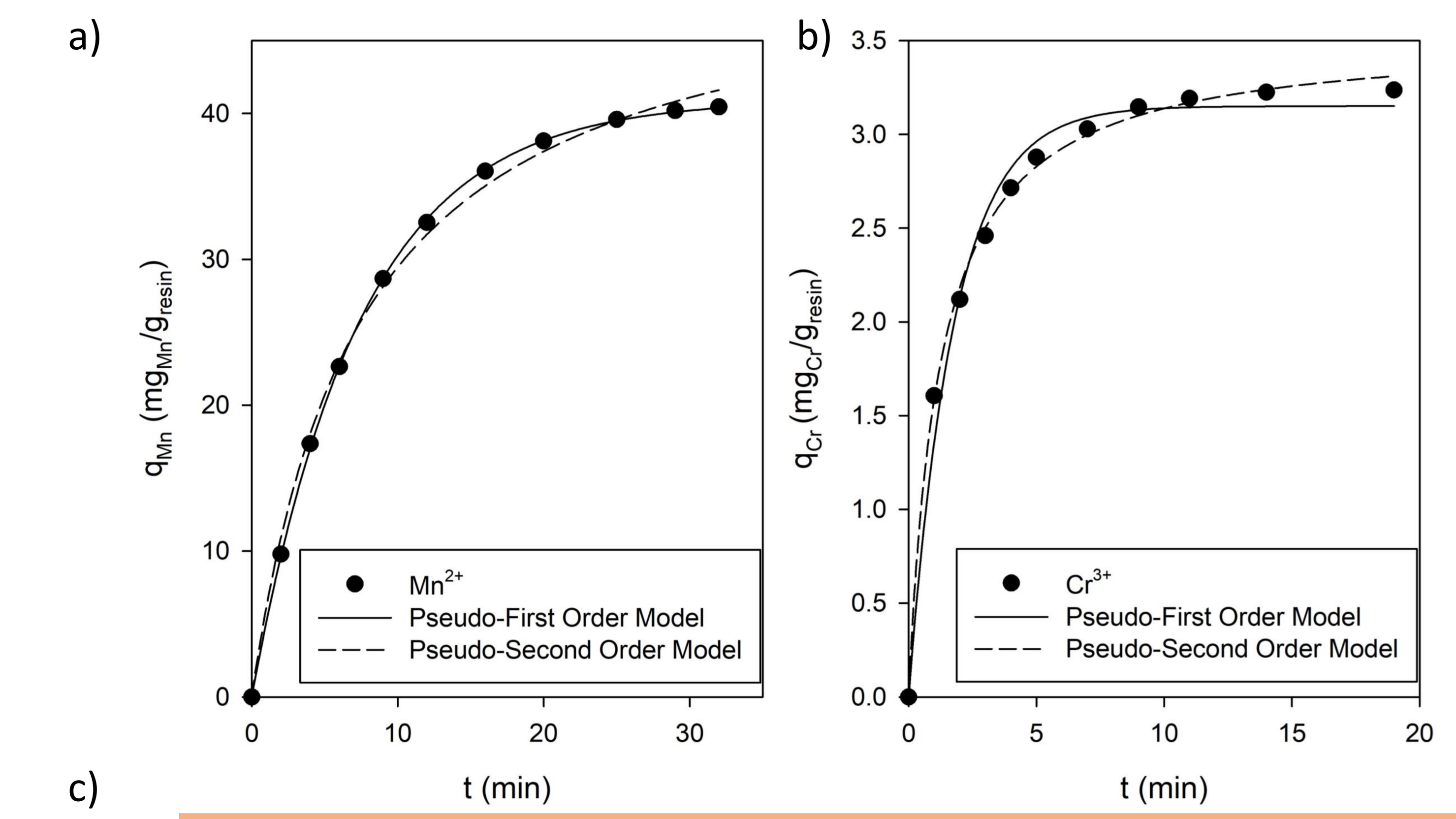
$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \quad (4)$$

With q_e, the equilibrium adsorption capacity; K_L the sorption equilibrium constant and C_e the concentration at equilibrium.

Kinetics

- Shaking at 500 rpm with NMR tubes filled with 5.5 mg of wet resin and 350 µl of 10mM (Mn^{2+});
- Shaking at 500 rpm with NMR tubes filled with 45 mg of wet resin and 350 µl of 6.95mM (Cr^{3+});
- Measurement of T_2 (20mHz) at different time intervals;
- Calculation of q with (1);
- Fitting Kinetic data with Pseudo-First (2) and Pseudo-Second Order model (3).

Study of Cr(III) and Mn(II) loaded resin by benchtop nuclear magnetic resonance.



c)

	Pseudo First-order		Pseudo-Second order	
	$q_{e,F}$ (mg g^{-1})	K_1 (min^{-1})	$q_{e,S}$ (mg g^{-1})	K_2 (g mg^{-1} min^{-1})
Mn(II)	40.9	0.13	51.2	2.6 10^{-3}
Cr(III)	3.15	0.6	3.5	0.23

Figure 2. Fitting of the kinetics data with a Pseudo-First and Pseudo-Second order model for (a) Mn^{2+},(b) Cr^{3+} adsorption by Dowex Marathon MSC at 22°C. (b) Results of the fitting for Mn^{2+} and Cr^{3+}.

Isotherms

- Repeating the same experiment with different metal concentrations;
- Measurement of T_1 and T_2 when equilibrium was reached;
- Calculation of q_e with (1) and fitting isotherm with Langmuir model (4).

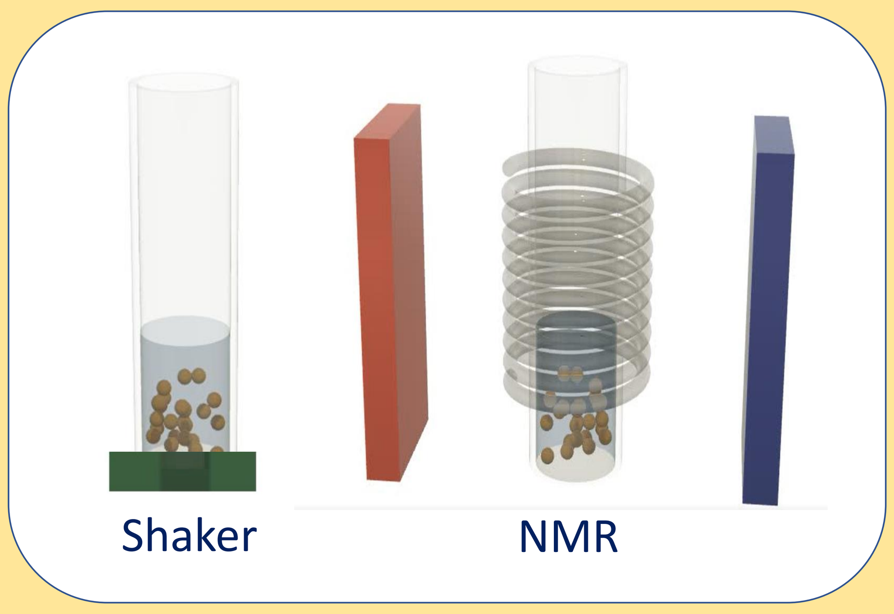
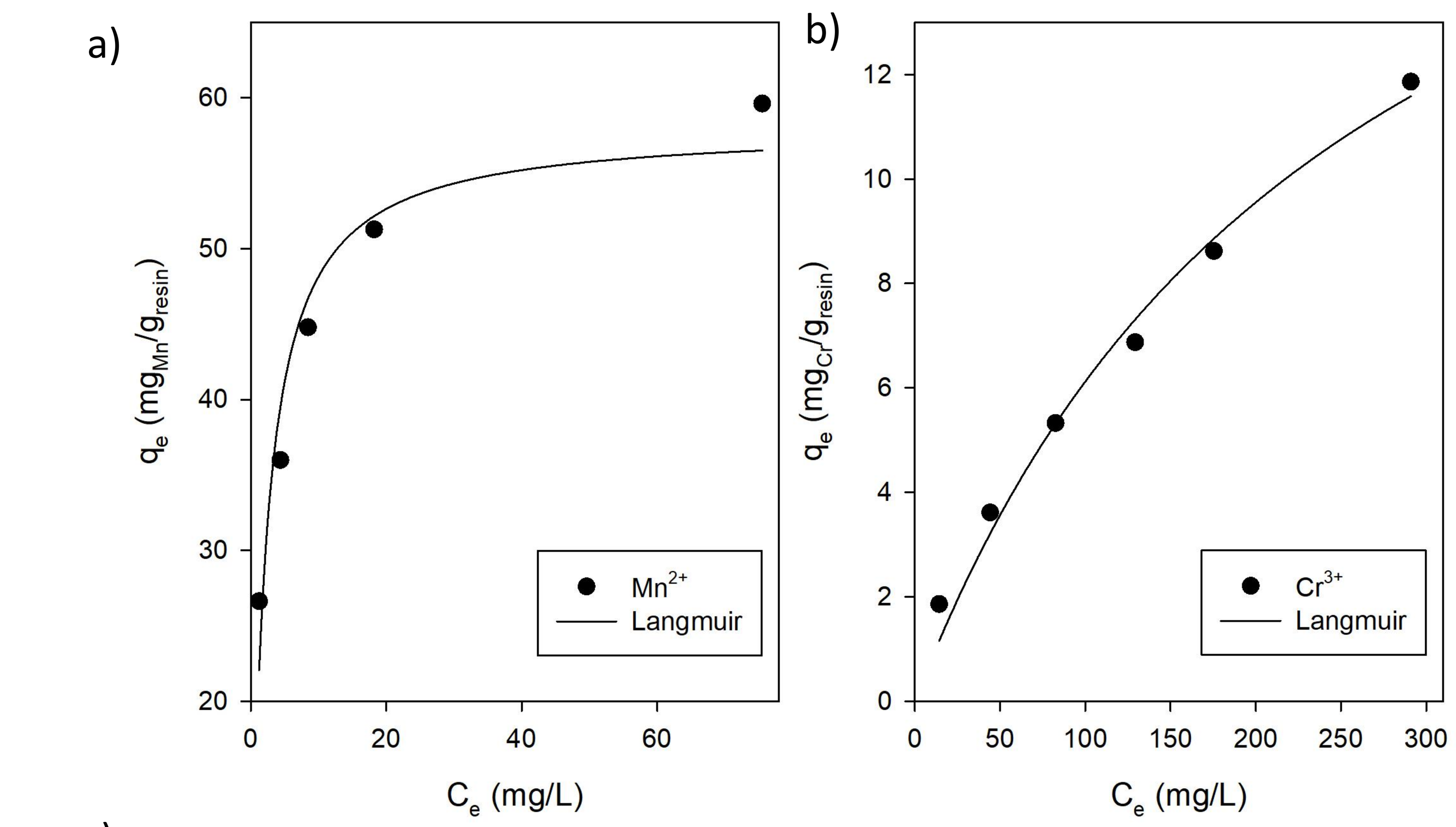


Figure 1. Experimental Set-up



c)

	Langmuir		
	q_{max} (mg g^{-1})	K_L (L mg^{-1})	R^2
Mn(II)	58.1	4.9 10^{-1}	0.93
Cr(III)	21.8	3.9 10^{-3}	0.98

Figure 3. Fitting of adsorption isotherm with the Langmuir model of (a) Mn^{2+},(b) Cr^{3+} on Dowex Marathon MSC at 22°C. (c) Results of the fitting.

The next step will be to reproduce these experiments with other adsorbents like activated carbon and at different magnetic fields. In the future, it will also be interesting to carry out a so-called NMR column experiment in order to follow the loading of resin in real-time through the measurement of the NMR signal.

[1] Tchounwou, P. B., Yedjou, C. G., Patlolla, A. K., & Sutton, D. J., Molecular, Clinical and Environmental Toxicology. Experientia Supplementum,101, 133-164 (2012).
[2] Gossuin, Y., Hantson, A.-L., & Vuong, Q. L, Journal of Water Process Engineering, 33, 101024 (2020).
[3] Gossuin, Y., & Vuong, Q. L., Separation and Purification Technology, 202, 138-143 (2018).

This work was supported by the Fonds de la recherche scientifique-FNRS under Grant n° T.0113.20