Benchtop NMR relaxometry to monitor Ni(II) removal by resin and activated charcoal

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Context

Heavy metals ions such as Ni^{2+} 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 adsorbent [2-3]. In this research, the removal of Ni^{2+} by Dowex Marathon MSC resin and commercial activated carbon (AC) was studied with T_1 and T_2 relaxometry. T_1 measurements of Ni^{2+} solutions after adsorption/ion exchange were used to obtain adsorption/ion exchange isotherms. Study of the relaxation time of the loaded resin/AC was also performed.

Isotherms

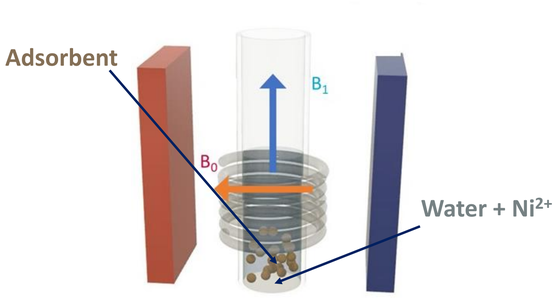

Fig. 1 Experimental set-up for adsorption/ion exchange isotherm

Method

- Shaking at 300 rpm with NMR tubes filled with 5.5 mg of wet resin (50 mg of AC) and 350 µl of Ni^{2+} solution at different concentrations;
- Measurement of T_1 at 22 °C and 20 MHz when equilibrium was reached;
- Calculation of q_e, C_e with Eq. 1 and 2;
- Fitting isotherm with Langmuir and Freundlich model (Eq. 3 and 4).

NMR

Model

From the value of T_1 or T_2 measured, the concentration of Ni^{2+} remaining in solution (C) can be determined with:

$$C = \frac{\left(\frac{1}{T_{i,\,water}} - \frac{1}{T_i}\right)}{r_i} \quad (1)$$

Where subscript *i* denotes 1 or 2; $T_{i,\,water}$, the relaxation time of water and r_i, the relaxivity.

The amount of Ni^{2+} loaded on the adsorbent (q) can be obtained with:

$$q = \frac{VA}{m}[C_0 - C] \quad (2)$$

Where V, the volume of solution; A, the atomic weight; C_0, the initial ion concentration; and m, the mass of adsorbent.

ISOTHERMS

Adsorption/ion exchange isotherms are generally described by the Langmuir isotherm model. This model predicts the maximum adsorption capacity (q_{max}) of an adsorbent for Ni^{2+} ion:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \quad (3)$$

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

Another common model for the Ni^{2+} adsorption/ion exchange isotherms is the Freundlich model:

$$q_e = K_F C_e^{1/n} \quad (4)$$

Where K_F is an adsorption capacity constant and n is the adsorption intensity.

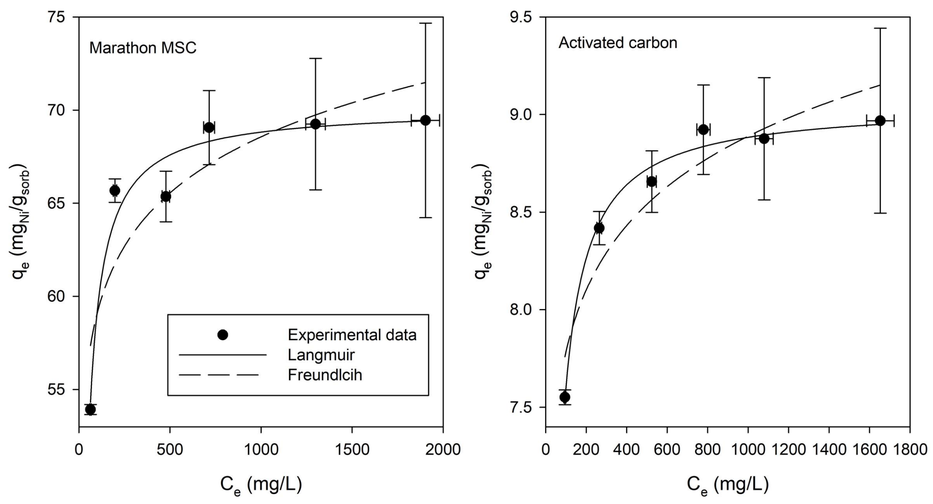

Fig. 2 Fitting of Langmuir and Freundlich isotherms for Ni^{2+} capture with Dowex Marathon MSC and AC

Table 1 Parameters of Langmuir and Freundlich models

	Langmuir		
	q_{max} ($mg_{Ni}\ g_{sorb\text{-}1}$)	K_L ($[L\ mg_{Ni}^{-1}] \times 10^{-2}$)	R^2
Marathon MSC	70.1 ± 0.8	5.4 ± 0.7	0.96
AC	9.1 ± 0.1	5.22 ± 0.31	0.99

	Freundlich		
	K_F ($mg_{Ni}^{1-1/n}\ g_{sorb}^{-1}\ L^{1/n}$)	n	R^2
Marathon MSC	43.8 ± 0.8	15.4 ± 4	0.9
AC	5.96 ± 0.38	17.3 ± 3.1	0.9

Loaded adsorbent

Method

- Shaking with magnetic stirrer, beakers filled with 10 g of wet resin (1 g of AC) and 25 mL of Ni^{2+} solution at different concentrations;
- When equilibrium is reached, rinsing and filtration of the loaded adsorbent before drying it;
- Filling NMR tubes with 2 g of loaded Dowex and 80 mg of loaded AC rehydrated with distilled water (4 mL for Dowex; 200 µL for AC);
- For AC only, filtration by centrifugation in order to remove the intergranular water [4];
- Measurement of T_1, T_2 at 10 MHz for resin (at 20 MHz for AC) and 22 °C;
- Mineralization of the loaded adsorbent prior to determination of its Ni^{2+} content thanks to inductively Coupled Plasma (ICP) Atomic Emission Spectroscopy/Mass Spectrometry (AES/MS) technique.

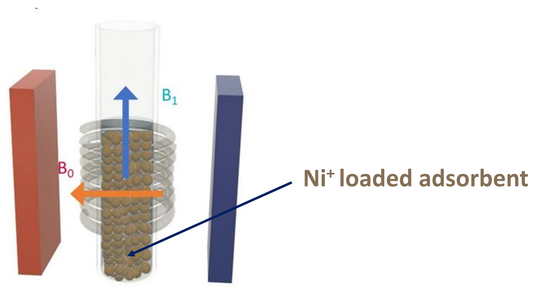

Fig. 3 Experimental set-up for the study of the loaded adsorbent

T_1 and T_2 curves of the Ni^{2+} loaded AC post-filtration are biexponential
loaded resin are biexponential

For resin

***1/T*$_{i,\,slow}$** are related to **interporosity**
***1/T*$_{i,\,fast}$** are related to **intraporosity**

$1/T_{i,\,slow}$ and $1/T_{i,\,fast}$ can be correlated with the Ni^{2+}content determined by ICP-AES/MS. The data was fitted using an empirical law:

$$1/T_i = a q_{ICP}^c + b \quad (5)$$

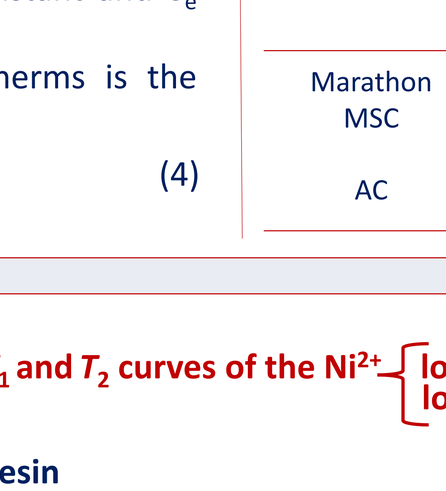

Fig. 4 Effect of Ni^{2+} content on the relaxation rates of the fast-relaxing fraction of Dowex Marathon MSC.

For AC (post-filtration)

***1/T*$_{i,\,slow}$** are related to **mesoporosity**
***1/T*$_{i,\,fast}$** are related to **microporosity**

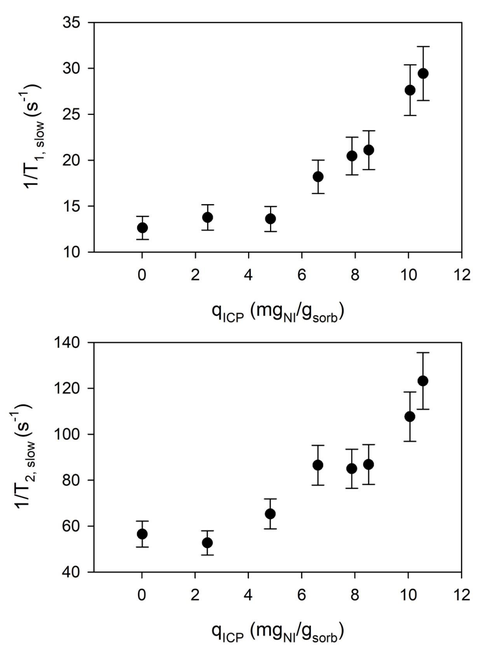

Fig. 5 Effect of Ni^{2+} content on the relaxation rates of the slow-relaxing fraction of AC after filtration by centrifugation

The next step will be to carry out a so-called NMR column experiment in order to follow the loading of adsorbent in real-time through the measurement of the NMR signal.

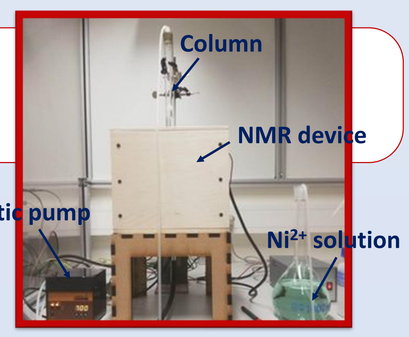

Fig. 6 Set-up for column experiment

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