Study of heavy metal loaded resins by benchtop NMR

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BIOPHYS

Abstract

Heavy metals discharged by industrial wastewater to the environment have become a major public health and environmental concern [1]. For example, heavy metals ions such as Ni (II) and Cu (II) are known to be toxic and must be removed from wastewater. However, these ions have also paramagnetic properties which previously allowed the use of Magnetic Resonance Imaging (MRI) and Nuclear Magnetic Resonance (NMR) relaxometry to follow their migration and their adsorption on different media [2, 3]. The goal of this study is to monitor the removal of Ni (II) and Cu (II) from water by amberlite IR120 with T_1 and T_2 relaxometry.

Set-up

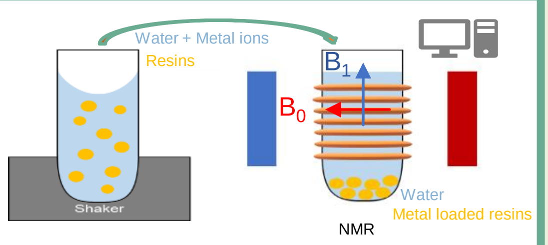


Figure 1. Experimental set-up.

Model Isotherm

From the value of T_1 or T_2 measured at equilibrium, the amount of heavy metals ions adsorbed on resin (q_e) and the concentration in the solution (C_e) can be determined with :

$$q_e = \frac{V_{sample}\, A_{ion}\left([ion]_{ini} - \left(\frac{C_e}{\frac{\frac{1}{T_i} - \frac{1}{T_i^{water}}}{r_i}}\right)\right)}{m_{resin}} \qquad (1)$$

With V_{sample}, the volume of solution; A_{ion}, the atomic weight; $[ion]_{ini}$, the initial ion concentration; r_i, the relaxivity and m_{resin}, the mass of resin.

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

$$q_e = \frac{q_{max} K_L\, C_e}{1 + K_L C_e} \qquad (2)$$

With K_L the sorption equilibrium constant.

Isotherm

- Shaking during 4h with NMR tubes containing 350µl of different $[Ni^{2+}]$ solutions and 5.5mg of wet resin,
- Measurement of T_1,T_2 at 28MHz
- Calculation of q_e and C_e with (1),
- Fitting isotherm with Langmuir model (2).

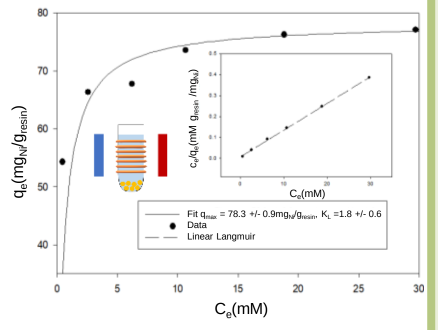
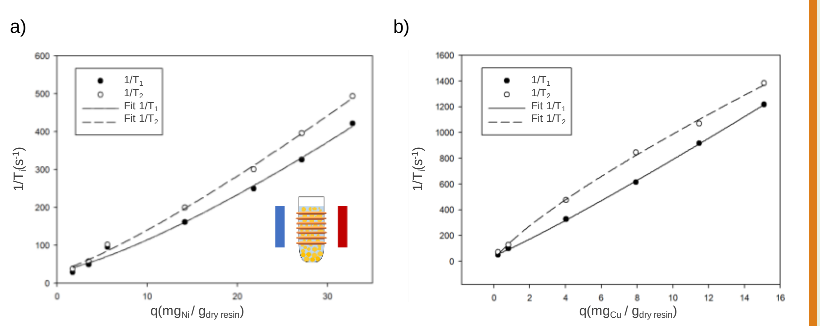


Figure 2. Fitting of adsorption isotherm with the Langmuir model of Ni^{2+} on Amberlite IR120 at 22°C and pH = 4.

Loaded resin



c)

F(q) = aq^n +b				
		a (g_{resin}^n / s mg_{metal}^n)	b (s^{-1})	n
Ni^{2+}	T_1	4.1	32.9	1.32
	T_2	6.64	31.9	1.23
Cu^{2+}	T_1	59.6	45.5	1.09
	T_2	146	18.5	0.82

Figure 3. Effect of the (a) Ni^{2+},(b) Cu^{2+} content of amberlite IR120 resin on the fast relaxation rates $1/T_i$ of the wet resin at 22°C. (c) Results of the fitting with an empirical law F(q) = aq^n +b

- Shaking during 8h with beakers containing 10mL of different $[Ni^{2+}]$, $[Cu^{2+}]$ solutions and 1g of wet resin then drying during 5h at 70°C,
- Preparation of NMR tubes with 0.2g of the dry resin and 200µl of deionized water,
- Measurement of T_1,T_2 at 28MHz.
- Correlation between the fast relaxation rates of the biexponential relaxation curves and the metal content of the dry resin measured by ICP-AES.

Conclusion

The NMR experiments allow to determine a maximum adsorption capacity of 78.3mg g^{-1} and 81.5mg g^{-1} for Ni(II) and Cu(II) respectively whereas the sorption equilibrium constants are 1.8mM^{-1} (Ni^{2+}) and 0.98mM^{-1} (Cu^{2+}).The next step will be to reproduce these experiments for other resins, adsorbents and paramagnetic ions in different conditions (e.g., different magnetic fields, temperatures, pH).

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