Study of heavy metal removal by benchtop NMR

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Abstract

Water pollution by heavy metals is a major environmental concern [1]. Adsorption is one of the most used and promising heavy metal removal techniques. However, current techniques to study the adsorption efficiency are indirect and destructive. In this research, the paramagnetic properties of some heavy metal present in wastewater (Cu (II), Ni (II), Mn (II), Cr (III)) are used. Indeed, it is well known that paramagnetic ions affect the Nuclear Magnetic Resonance (NMR) relaxation times of water protons, which can be measured by benchtop NMR relaxometry [2-3]. Therefore, the purpose of this study is to prove the abilities of direct and non-destructive NMR relaxometry to monitor the removal of paramagnetic heavy metals in batch experiment by ion exchange resins.

Set-up

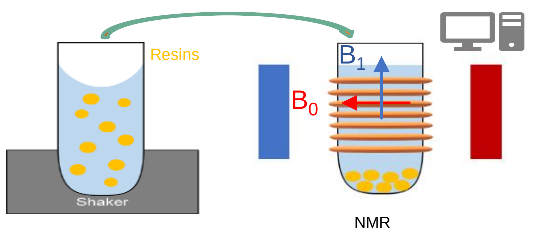

Figure 1. Experimental set-up.

Model

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

$$q = \frac{V_{sample}\, A_{ion} \left([ion]_{ini} - \overbrace{\left(\frac{\frac{1}{T_i} - \frac{1}{T_i^{water}}}{r_i} \right)}^{c} \right)}{m_{resin}} \quad (1)$$

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 kinetic of adsorption can be described by the pseudo-second order kinetic model:

$$\frac{t}{q} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \quad (2)$$

where q_e are the amounts of adsorbate adsorbed at time t and at equilibrium, k_2 is the equilibrium rate constant.

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

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

With K_L the sorption equilibrium constant.

Kinetic

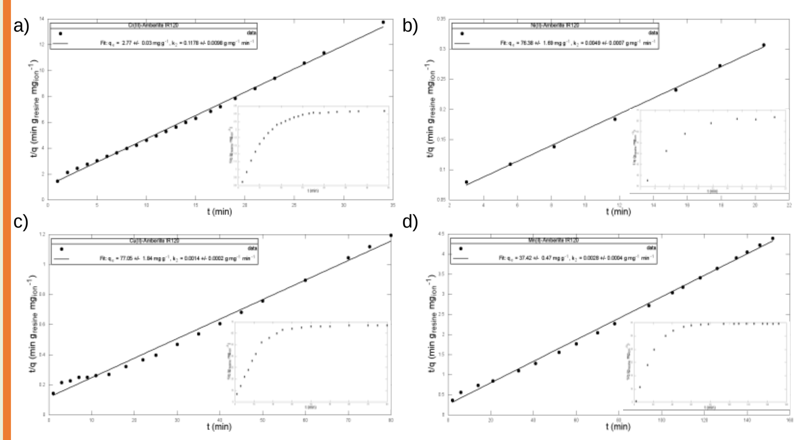

Figure 2. Fitting of the kinetics data with a pseudo-second-order model for (a) Cr^{3+}, (b) Ni^{2+}, c) $Cu^{2+}$and (d) Mn^{2+} removal by Amberlite IR120 resin at T=20°C.

Isotherm

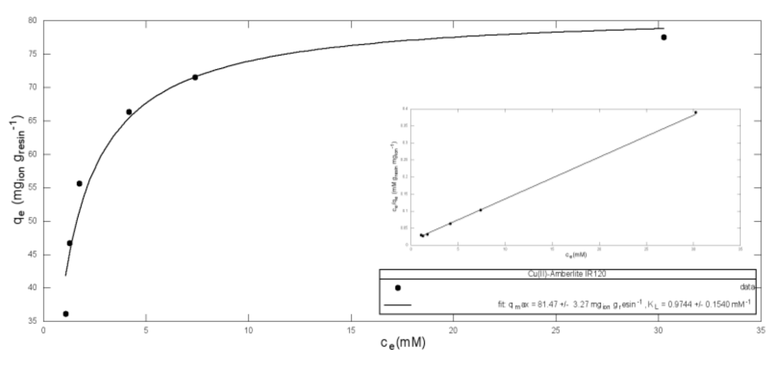

Figure 3. Fitting of adsorption isotherm with the Langmuir model of Cu^{2+} on Amberlite IR120 at 22°C and pH=4.

Conclusion

The NMR experiments allow to determine a maximum adsorption capacity of 81.5 mg g^{-1} and 7.9 mg g^{-1} for Cu(II) and Cr (III) respectively whereas the sorption equilibrium constant are 1 L mg^{-1} (Cu^{2+}) and 0.6 L mg^{-1} (Cr^{3+}). Experimental kinetic data fitted well with the pseudo-second-order kinetic model.The next step will be to reproduce these experiments for other adsorbents and paramagnetic ions in different conditions (e.g., different magnetic fields, temperatures, pH).

[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).

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