SYNTHESIS OF MONTMORILLONITE-ALGINATE BEADS APPLIED TO THE KINETIC STUDY OF PARAQUAT ADSORPTION

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1. Introduction

Paraquat (1′-dimethyl-4,4′-bipyridinium dichloride, PQ) is a quaternary ammonium herbicide. Although its use is restricted within the European Union, as it is considered a highly hazardous pesticide (HHP), it is still used worldwide, so further research into this pollutant is needed. Water pollutants removal is mainly carried out by adsorption processes. These processes require the use of adsorbents with some features such as low cost, accessibility and non-toxicity. Alginate (Alg) - Montmorillonite (Mt) beads have been effective for the adsorption of PQ [1].

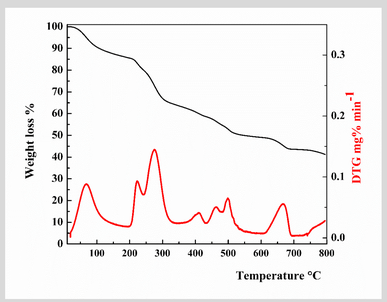
The aim of this work is synthesise and characterise alginate beads loaded with a 70 % of montmorillonite (Alg-Mt70) at different resident times in $CaCl_2$ in order to analyse the effect of the ionic gelation process on the PQ adsorption process. In addition, the adsorption kinetic of the pollutant paraquat on Alg-Mt70 beads was evaluated.

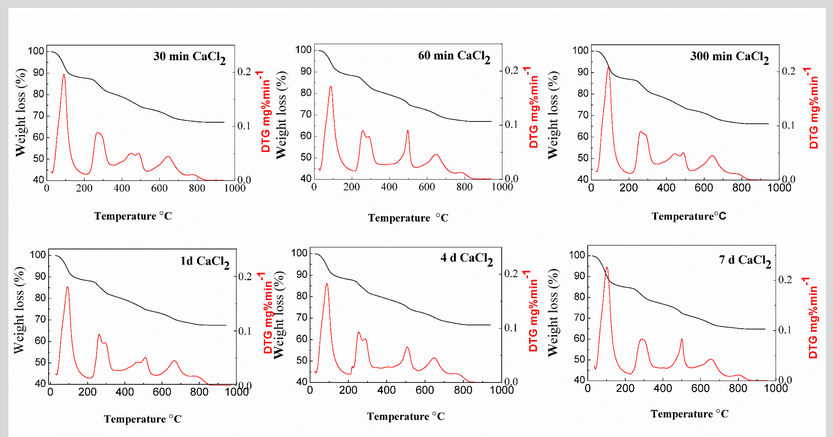
2. Materials and Methods

Beads were synthesized by dissolving sodium alginate in 0.1 M NaCl to form a 1.0 % by weight alginate solution. An amount of montmorillonite clay from natural deposits in Argentina was added to this solution and the mixture was homogenized on a mechanical stirrer overnight. This homogenized solution was added dropwise to a 0.1 M $CaCl_2$ solution with a peristaltic pump to produce calcium alginate-montmorillonite (Alg-Mt) beads. The residence times studied of the beads formed in this $CaCl_2$ solution were 30; 60; 120 minutes; 1; 4 and 7 days. . The beads were characterized by elemental composition, thermogravimetric analysis (TG-DSC) and scanning electron microscopy (SEM-EDX). After beads characterization, the adsorption of PQ as a function of time was studied for 3 initial concentrations of the herbicide (C_0 = 19, 38 and 50 ppm) on the beads with gelation times of 30 minutes and 7 days. The experimental results of herbicide adsorption as a function of time were fitted with the Shrinking Core Model (SCM) [2]. The concentration profile as a function of time was obtained.

3. Results and Discussion

3.1 Synthesis and characterization





Element	Surface bead % w/w	Internal bead % w/w
C	63.56	44.22
O	18.33	28.03
Al	4.81	7.25
Si	13.3	18.68
Mg	-	0.91
total	100	100

Sample	Elemental composition %		
	%C	%H	%N
Al-Mt0	16.51	3.38	<0.4
Alg-Mt70-30	5.29	2.15	<0.4
Alg-Mt70-60	5.18	2.12	<0.4
Alg-Mt70-120	4.97	2.00	<0.4
Alg-Mt70-1d	4.92	2.06	<0.4
Alg-Mt70-4d	5.18	2.24	<0.4
Alg-Mt70-7d	4.85	2.34	<0.4

3.2 Paraquat adsorption

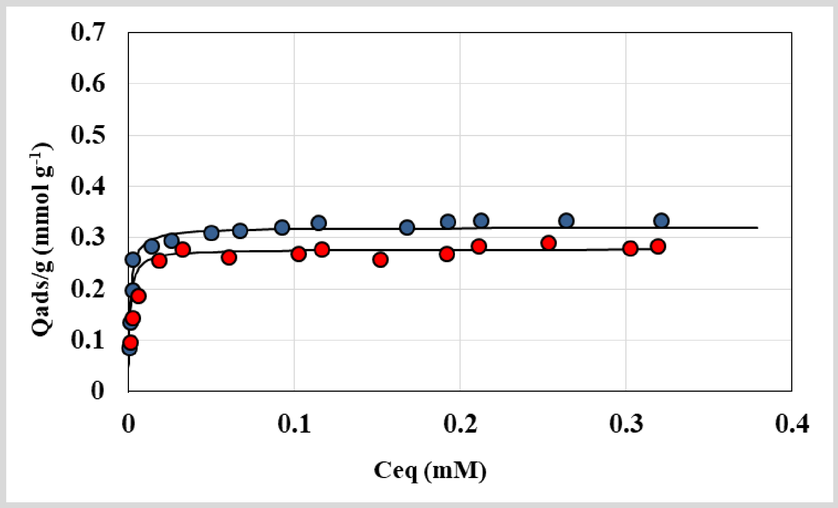


Figure 1. Adsorption isotherm of PQ onto the beads (Alg-Mt70 30 min ● and Alg-Mt70 7 d ●)

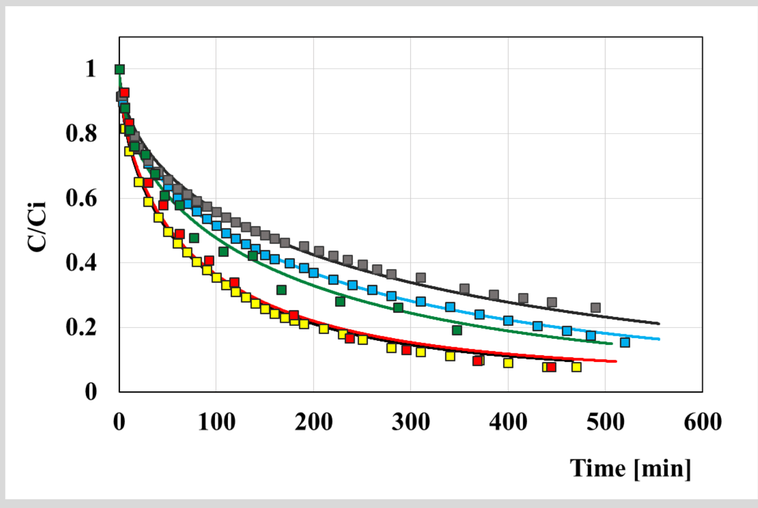


Figure 2. Concentration profile as a function of time.
Fits are made by the shrinking core model

Alg-Mt70 30 min Ci = 19 ppm ■ Alg-Mt70 30 min Ci = 38 ppm ■ Alg-Mt70 30 min Ci = 50 ppm ■
Alg-Mt70 7 d Ci = 19 ppm ■ Alg-Mt70 7 d Ci = 38 ppm ■

4. Conclusion

The results obtained showed a very good agreement between the model prediction and the experimental data. The effective diffusion coefficients of the adsorbent material were obtained as fitting parameters. No major differences were observed in the adsorption behaviour with the gelation time of the beads, so it can be concluded that Alg-Mt70 beads with only 30 minutes in $CaCl_2$ is a stable and efficient material for PQ adsorption, not requiring long gelation processes.

5. References

[1] Etcheverry M, Cappa V, Trelles J, Zanini GP. *Journal of Environmental Chemical Engineering* 2017, 5, 5868 – 5875.

[2] Dominguez MA, Etcheverry M, Zanini GP. *Adsorption* 2019, 25, 1387 - 1396.