



Copper and nitrophenol pollutants removal by Na-montmorillonite/alginate microcapsules

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ABSTRACT

The use of renewable bioresources allows the development of low cost adsorbents that are versatile. In the present paper, the affinity and the removal capacity of montmorillonite/alginate microcapsules for a hydrophobic organic pollutant (4-nitrophenol) and an inorganic pollutant (copper) were evaluated. The physicochemical processes through sorption and kinetic experiments under different ratios of montmorillonite vs. alginate and initial contaminant concentrations were investigated. The total weight loss and diameter decrease during the drying process were 90–96% and 64%, respectively. A significant decrease in beads diameter, related to water elimination, has been observed during the first 24 h. Structural modifications that occur during the drying process were evaluated using thermal analysis. From correlation coefficients, the second-order equation depicts properly the adsorption of copper by the microbeads adsorption capacity increases to saturation with time; 3 and 6 h were needed to reach equilibrium on wet and dry mixed microcapsules. The pseudo-second order model properly depicts the adsorption process of 4-NP onto Na-mont and (Na-mont/SA) mixed microcapsules but failed to reproduce the data observed for the alginate beads. Isotherms data were fitted with good correlation using the Langmuir model; alginate and montmorillonite adsorption capacities (q_m /wet beads) agree with those obtained by various studies.

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1. Introduction

The industrial growth and population increase have resulted in the release of different pollutants in the environment and the treatment of effluents has become a challenging topic in environmental sciences. Efforts are therefore still needed to have low cost adsorbents that are versatile e.g. high adsorption capacity of inorganic/organic pollutants. Alginate beads are common and well-known support materials in biosciences applications [1] and are now used in the environmental field [2,3]. Sodium alginate, a water-soluble salt of alginic acid, is a biopolymer and differs from most other polysaccharides exhibiting a sol–gel transition when simply submitted to modification of their ionic environment, e.g. substitution of sodium by divalent cations such as calcium. This material is biocompatible, low cost and the technique of encapsulating is simple [4]. Industrial processes in water treatment (e.g. filtration, fluidized bed) require granular materials of controlled size and the encapsulation of different components in the alginate beads to enhance the properties (e.g. adsorption capacity of organic/inorganic pollutants, mechanical properties, . . .) are widely

investigated [2,5–7]. For instance, aluminosilicates (natural or modified) are being tested for more than 20 years in the removal of toxic metals or organic pollutants [8,9] from aqueous solutions due to favourable surface properties, availability, environmental and economical considerations.

Objectives of the present work were to evaluate the uptake of an hydrophobic organic pollutant (nitrophenol) and a cationic inorganic pollutant (Cu^{2+}) by montmorillonite/alginate capsules using batch experiments. The effects of montmorillonite vs. alginate ratios, diffusion mechanisms and drying on pollutants uptake are investigated.

2. Materials and methods

2.1. Materials

Sodium alginate was purchased from Fluka and used without further purification. Solutions of this work were prepared by dissolution of calcium chloride (Fluka) 4-nitrophenol (4-NP, Fluka) and copper nitrate trihydrate (Sigma–Aldrich) in Milli-Q water. Volclay bentonite (>90% montmorillonite) from Sigma–Aldrich after sodium exchange was separated from solution, washed several times with Milli-Q water then dried and milled into a fine powder.

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Fig. 1. Beads photos (a) wet Na-mont/SA 2/1, (b) dry Na-mont/SA 2/1, (c) wet SA and (d) dry SA.

2.2. Preparation and characterization of montmorillonite/alginate microcapsules

One to four grams of exchanged montmorillonite (Na-mont) were dispersed in 100 ml of Milli-Q water. An alginate suspension (1%, w/w; $V = 100$ ml) was added and the mixture was stirred for 1 h. Once the mixture was homogeneous, it was forced through a micropipette tip by a peristaltic pump and the resulting droplets were collected in a stirred reservoir containing 200 ml of 0.1 M CaCl_2 [2]. The beads were filtered and washed several times with Milli-Q water. Ibanez and Umetsu [10] underlined the interest to use dried rather than gel microbeads: accurate measurement of the mass to be used, better handling nature, gain in mechanical strength and rigidity, and more favourable uptake of metal ions. The beads were used wet or after drying at 20 °C for 72 h.

Microcapsules were observed with a Nikon optical microscope equipped with a digital camera and a video monitor. Mean diameters were obtained from digitized photographs using an image analysis software (ImageJ). Apparent densities and volumes were determined respectively by pycnometry (AccuPyc 1330 pycnometer) and the volumetric displacement method. Thermogravimetric/differential thermal analysis curves were recorded using a Netzsch STA 409 apparatus from room temperature to 1000 °C. Microcapsules were mixed with pure potassium bromide, ground and pressed to form pellets. The pellets were analysed by FTIR spectroscopy (Perkin-Elmer Paragon 1000); the spectra were collected within the range of 400–4000 cm^{-1} .

2.3. Adsorption experiments

Sorption kinetics and isotherms experiments were studied in a batch mode at room temperature. Experiments were performed without pH adjustment and the initial pH values were 5.5 for 4-NP and 5 for copper. According to a previous report [11], $\text{p}K_a$ value of 4-NP at 30 °C is 7.15; molecular form of nitrophenol could be considered in adsorption experiments. Bayramoglu et al. [12] observed

maximum cationic metal adsorption between pH 5 and 6 using different alginate beads and precipitation of Cu^{2+} ions as $\text{Cu}(\text{OH})_2$ occurs at pH higher than 7 leading to an inaccurate interpretation of adsorption.

In all sets of experiments, 0.25 g of dry beads or 5 ml of wet beads were added to 100 ml of known 4-NP or copper concentrations. Nitrophenol and copper concentrations were determined at 318 nm by UV spectrophotometry (Varian Carry 50) and atomic absorption spectrophotometry (VarianSpectrAA 220), respectively.

3. Results and discussion

3.1. Characterization of the beads

The typical pictures of the capsules prepared in this study were shown in Fig. 1. Spherical capsules with an external diameter of about 3 mm (wet beads) and about 1 mm (dry bead) were found for SA entrapment with Na-mont or not. The introduction of Na-mont into SA capsules was easily confirmed from the color of the capsules. Apparent densities and diameters obtained for three different Na-mont/SA ratios and alginate beads are reported in Table 1. The drying process induced shrinkage of the microcapsules [13] and

Table 1
Microcapsules characteristics.

Na-mont/SA ratios (w/w)		Apparent density (g/cm^3)	Diameter (mm)
4/1	Dry	1.98	–
	Wet	1.05	–
2/1	Dry	1.90	0.99
	Wet	1.03	2.92
1/1	Dry	1.85	–
	Wet	1.02	–
0/1	Dry	1.67	1.00
	Wet	1.01	2.92

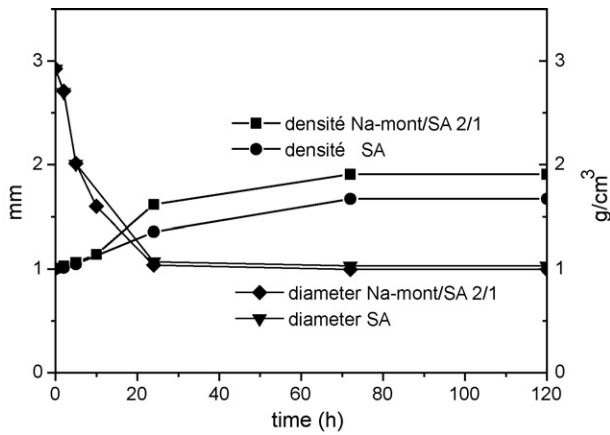


Fig. 2. Size and apparent density evolution during the drying process at 20 °C of SA and Na-mont/SA beads.

the weight loss and diameter decrease during the drying process were respectively 90–96% and 64% (Fig. 2). A significant decrease in beads diameter, related to water elimination, was observed during the first 24 h of drying process but during the next 48 h the diameter remained stable. In contrast, the density slightly increases during the 72 h of drying process.

Structural modifications that occur during a thermal process were evaluated using thermogravimetry and differential thermal analysis (TGA/DTA). Endothermic peak at 200 °C which occurs on the DTA curves (Fig. 3) of mixed Na-mont/SA microcapsules was attributed to the release of adsorbed water.

The two exothermic peaks around 430 and 520 °C are related to an additional step in the thermal degradation of SA. According to Cheong and Zhitomirsky [14], the thermal degradation of SA results to the formation of Na₂CO₃. Mass loss, recorded at 800 °C, was respectively 13%, 28% and 78% for Na-mont (Na-mont/SA, 2:1) and SA. This value for alginate gel beads is in a good agreement with the literature data [14].

The FTIR spectrum of Na-mont/SA (2:1) is shown in Fig. 4C. The broad band between 3200 and 3800 cm⁻¹ is attributed to Na-mont (Fig. 4A) e.g. OH stretching band typical of water adsorption on montmorillonite (shoulder: 3630 cm⁻¹) and alginate (Fig. 4B) e.g. stretching frequencies of OH groups (3416 cm⁻¹). Carboxylate asymmetric/symmetric stretching (1623 and 1428 cm⁻¹) [15], -C-O stretching of the ether group (shoulder: 1118 cm⁻¹) are attributed to alginate; -C-O stretching band of alcoholic group (1082 cm⁻¹) [16] has disappeared. In-plane stretching vibration of surface Si-O-Si

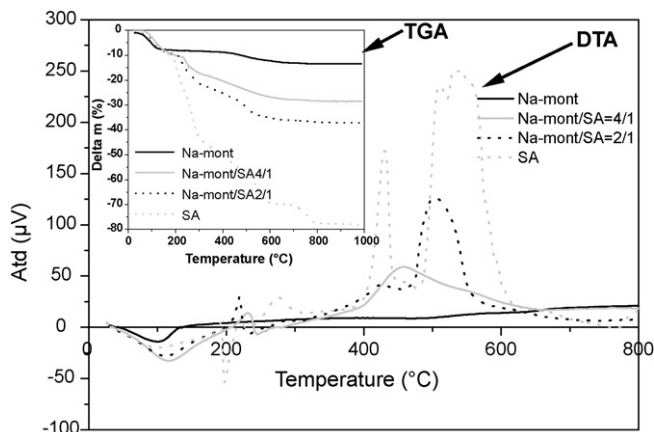


Fig. 3. TGA/DTA curves of the studied sorbent.

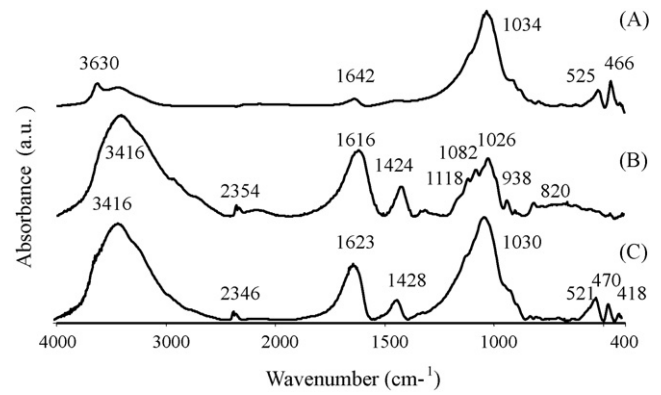


Fig. 4. FTIR spectra: (a) Na-mont, (b) SA and (c) Na-mont/SA (2:1, w/w).

(1034 cm⁻¹) and Si-O bending vibrations (525 and 465 cm⁻¹) [17] is attributed to montmorillonite.

3.2. Adsorption kinetics

Many kinetic models are available to better understand the behaviour of adsorbents and to investigate the mechanisms controlling adsorption. Adsorption data were analyzed using the model pseudo-second order kinetic (1):

$$\frac{dq_e}{dt} = k_2(q_e - q_t)^2 \quad (1)$$

where q_e and q_t are the quantities adsorbed (mg g⁻¹) at equilibrium and at time t , respectively and k_2 is the rate constant of second order adsorption (g mg⁻¹ min⁻¹).

The pseudo-second order model properly depicts the adsorption process of the two pollutants except the data related to the sorption of 4-NP onto alginate beads (Table 2). Encapsulation unfavoured the sorption since the highest rate constants were observed for Na-mont. A double mechanism of diffusion in the gel structure and ion exchange was proposed to describe the kinetic of sorption of metals [18,19,24].

Pseudo-second order rate constants observed for dry beads were lower than those observed for wet materials. Dried natural hydrocolloids materials form a stable matrix with high porosity. This could delay the diffusion of solutes across the polymeric chains [5,20].

The adsorption of 4-NP onto alginate at the experimental pH is driven by a surface complexation mechanism and the kinetic model seems better fitted with the description of ion exchange mechanism. Two hours were needed to reach adsorption equilibrium for wet microcapsules, indicating that either the adsorption is taking

Table 2

Rate constants for kinetic adsorption of studied solutes on beads and Na-mont.

Adsorbents	Pseudo-second order			
	Cu ²⁺		4-NP	
	k_2 (g mg ⁻¹ min ⁻¹)	R^2	k_2 (g mg ⁻¹ min ⁻¹)	R^2
Wet				
SA	0.004 ± 0.002	0.99	0.32 ± 0.05	0.85
Na-mont/SA 1/1	0.006 ± 0.002	0.99	0.16 ± 0.01	0.91
Na-mont/SA 2/1	0.009 ± 0.008	0.99	0.030 ± 0.001	0.97
Na-mont/SA 4/1	0.012 ± 0.009	0.99	0.011 ± 0.001	0.99
Dry				
SA	0.0015 ± 2.10 ⁻⁴	0.97	0.036 ± 0.009	0.80
Na-mont/SA 1/1	0.0012 ± 2.10 ⁻⁴	0.97	0.008 ± 0.003	0.92
Na-mont/SA 2/1	0.0013 ± 2.10 ⁻⁴	0.97	0.011 ± 0.003	0.95
Na-mont/SA 4/1	0.0010 ± 2.10 ⁻⁴	0.96	0.007 ± 0.001	0.96
Na-mont	0.082 ± 0.023	0.98	0.091 ± 0.026	0.98

Table 3
Adsorption isotherm constants of adsorption of the studied pollutants.

Adsorbents	Cu ²⁺			4-NP		
	q_m (mg g ⁻¹)	K_L (L mg ⁻¹)	R^2	q_m (mg g ⁻¹)	K_L (L mg ⁻¹)	R^2
Wet						
SA	92.5 ± 1.8	0.075 ± 0.005	0.99	15.0 ± 1.2	0.036 ± 0.007	0.97
Na-mont/SA 1/1	60.6 ± 2.7	0.063 ± 0.009	0.97	26.4 ± 1.3	0.017 ± 0.002	0.99
Na-mont/SA 2/1	42.3 ± 2.0	0.050 ± 0.007	0.97	32.9 ± 3.4	0.014 ± 0.002	0.98
Na-mont/SA 4/1	29.5 ± 1.6	0.078 ± 0.014	0.95	34.3 ± 0.9	0.025 ± 0.001	0.99
Dry						
SA	72.9 ± 2.4	0.094 ± 0.009	0.99	9.7 ± 3.6	0.005 ± 0.005	0.89
Na-mont/SA 1/1	47.2 ± 2.1	0.102 ± 0.016	0.98	22.1 ± 1.5	0.014 ± 0.002	0.98
Na-mont/SA 2/1	39.2 ± 2.1	0.085 ± 0.017	0.98	29.8 ± 1.9	0.010 ± 0.001	0.99
Na-mont/SA 4/1	28.8 ± 2.9	0.054 ± 0.017	0.97	30.1 ± 1.8	0.012 ± 0.001	0.99
Na-mont	20.4 ± 1.0	0.839 ± 0.171	0.96	54.18 ± 4.0	0.027 ± 0.004	0.98

place on the particles surface or that diffusion within the structure is fast. The uptake of 4-NP onto the dry beads slows down after 4 h and the time needed to reach equilibrium was 16 h. Previous test of phenol derivatives adsorption on alginate microcapsules suggested 12 h [21].

3.3. Adsorption isotherms

Isotherms data were fitted with the Langmuir model (Table 3) describing the sorbent surface as homogeneous assuming that all the sorption sites have equal affinity and that sorption at one site does not affect sorption at an adjacent site. The Langmuir model can be expressed by

$$q_e = q_m \frac{bC_e}{1 + bC_e} \quad (2)$$

where q_e is the amount of solute adsorbed (mg g⁻¹), C_e is the equilibrium concentration of adsorbate (mg L⁻¹); q_m and b are Langmuir constants related to adsorption capacity and energy of adsorption, respectively.

The adsorption capacities of Cu²⁺ onto different adsorbents were ranked as follows: SA bead > Na-mont/SA 1/1 > Na-mont/SA 2/1 > Na-mont/SA 4/1 ratio beads > Na-mont. Due to the dissociation of carboxyl groups, alginate beads have many negative charges able to attract cationic Cu²⁺ species leading to an adsorption increase [22]. This was supported by the IR spectra of the alginate beads (Fig. 3); the cross-linking reactions poorly affected the carboxyl groups (1623 and 1428 cm⁻¹) responsible for the adsorption of divalent cations. Alginate and montmorillonite adsorption capacities (q_m /wet beads) agree with those obtained by various workers (Table 4). As mentioned in the literature, alginate, a polysaccharide biopolymer, has a significant high affinity to divalent metal ion (copper) whereas montmorillonite acts preferentially as an organic compound sorbent.

Additivity curves, obtained by mathematical addition of the theoretical sorption capacities for each mass of materials (alginate, Na-montmorillonite) contained in the mixtures fit with the copper experimental isotherms (wet and dry beads) especially for the adsorption onto Na-mont/SA 1/1 ratio (Figs. 5 and 6). In contrast, additivity curves failed to reproduce 4-NP data (Figs. 7 and 8).

Table 4
Adsorption capacity—literature results (comparative study).

Adsorbents	Pollutant	q_m (mg g ⁻¹)	Ref.
Alginate beads	Cu ²⁺	95	[23]
Alginate beads	Cu ²⁺	106	[24]
Alginate beads	Cu ²⁺	84	[25]
Alginate beads	Cu ²⁺	75–80	[10]
Na-mont	4-NP	28	[26]
Alginate/activated carbon beads	Cu ²⁺	175	[27]

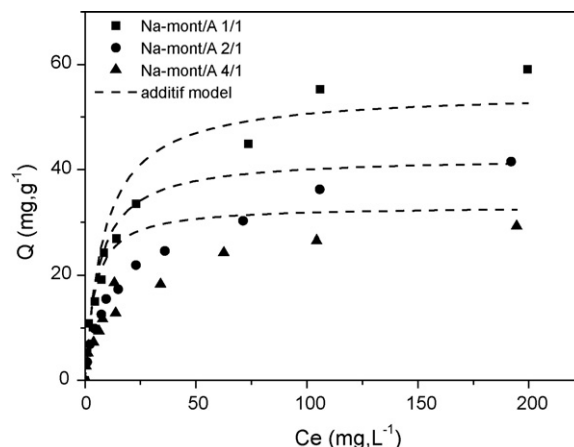


Fig. 5. Experimental point and curves of additivity model for adsorption capacity of Cu²⁺ on wet beads.

Adsorption of 4-NP on wet beads was additional for low concentrations (Fig. 7) but was no longer additional for higher concentrations. Access to sites is reduced and theoretical values were in all case higher than the experimental values. The encapsulation cause a part of the montmorillonite surface to be blocked for 4-NP but dehydration and modification of alginate structure by drying do not amplify this phenomenon. Additive adsorption is not totally achieved, but the production of a composite material by encapsulation of clay in alginate matrix give a granular adsorbent with a good contribution of each component.

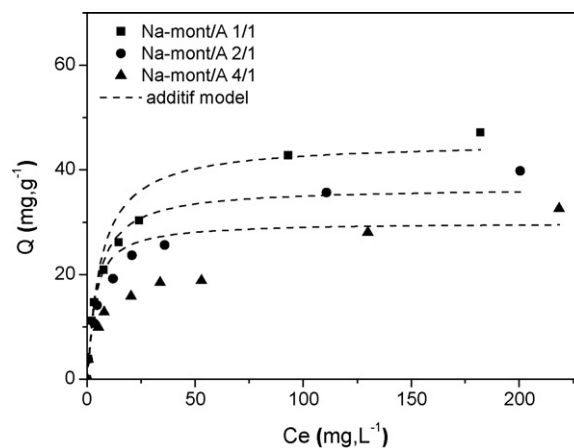


Fig. 6. Experimental point and curves of additivity model for adsorption capacity of Cu²⁺ on dry beads.

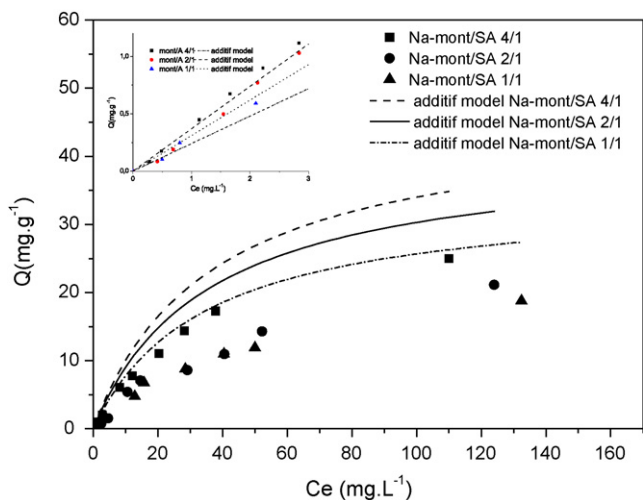


Fig. 7. Experimental point and curves of additively model for adsorption capacity of 4-NP on wet beads.

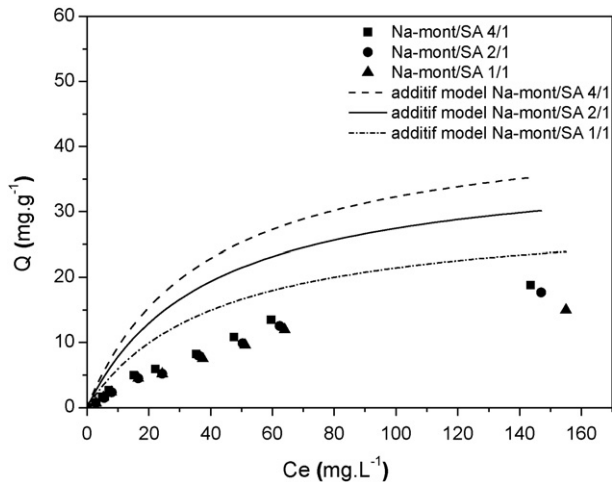


Fig. 8. Experimental point and curves of additively model for adsorption capacity of 4-NP on dry beads.

4. Conclusion

The beads obtained from the encapsulation of mixture Na-mont/SA are able to adsorb the 4-NP and Cu^{2+} contained in an aqueous solution. The 4-NP adsorption rises with the proportion of montmorillonite in the composite materials while the adsorption of Cu^{2+} increase with the alginate fraction. A combined adsorption of 4-NP and copper can be considered. Speed of adsorption onto montmorillonite is reducing by the encapsulation and for all materials, the gel diffusion controls the kinetic. Drying of the beads modifies their structure and decreases the kinetics constant for Cu^{2+} or 4-NP. The adsorption capacity of copper onto alginate or montmorillonite/alginate microcapsules is not modified by the encapsulation for the high concentrations of solute but weakly by the drying. The adsorption capacity of 4-NP is strongly affected by the encapsulation but the drying do not amplify this reduction. Using of granular composite adsorbent can be investigated with a contribution of each component, clay and alginate, to the treatment of organic/inorganic polluted water.

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