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Research paper

Montmorillonite-alginate beads: Natural mineral and biopolymers based sorbent of paraquat herbicides

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ABSTRACT

Beads of alginate montmorillonite have been used for the first time as sorbent of the cationic pesticide paraquat (PQ). They are a green material because they are formed by a biopolymer and a clay mineral, and because they allow using an energy efficient process to separate the beads after PQ adsorption. The general characterization of the beads, with montmorillonite contents ranging from 0% to 70%, has been carried out by elemental composition, FTIR and thermal analysis. The shape, external morphology and internal structure of the beads were examined by SEM. Wet beads were also observed with a digital camera. PQ adsorption was studied with adsorption isotherms from aqueous solutions, and maximum adsorption capacities (Q_{max}) were 0.093, 0.146, 0.187 and 0.278 mmol g^{-1} for montmorillonite contents of 0, 5, 30 and 70%, respectively. Q_{max} varied linearly with the clay content. The results show that montmorillonite is practically the only PQ sorbent, with alginate acting mainly as support of the clay particles, but playing a very important role allowing an effortless handling of the material and the adsorbed pollutant.

1. Introduction

Herbicides are continuously used to minimize the loss of crop productivity, but more than 99.9% of the applied pesticides move into the environment where they can adversely affect beneficial biota and contaminate soil, water, and the atmosphere [1]. Paraquat dichloride (PQ; 1,1-dimethyl-4,4-bipyridium dichloride) is a toxic quaternary ammonium herbicide and is widely used in agriculture as a non-selective agent for controlling broadleaf [2]. Introduced in the 1960s, PQ has now been banned in some countries because of its toxicity [3,4]. However, it is used in USA and several countries of South America, Australia, Asia, etc., which still permit that this agent to be used for example in chemical desiccation [5], controlling weeds in broad-acre cropping[6,7], rice field crops [8], etc.

The LD50 of PQ in humans is approximately 3–5 mg/kg, which translates into as little as 10–15 mL of a 20% solution. If PQ has been ingested in any amount it is necessary immediately administer an adsorbent. A clay suspension as Bentonite (7.5%) is highly effective [9].

Various techniques are being used to remove pollutants from aqueous waste [10,11], with sorption being one of the most promising technologies for water purification. The most widely used adsorbents in this concern include clay minerals [12], activated carbon [13] and polymers [14,15]. Thus, there is a growing interest in the use of bio-based materials such as polymers obtained from natural resources due to their environmentally friendly properties and renewable abundance [16–18].

The adsorption studies of PQ on materials easy to handle and nontoxic are important for cleaning water and as a therapeutic measure in case of intoxication. Alginate beads are a well-known support material in bioscience application [19] for immobilization of enzymes [20] and living cells [21]. Over the past few years they are being used in the environmental field for the removal of some heavy metal ions and organic pollutants [22–25]. The capacity of alginate to form gel in the presence of multivalent cations (ionotropic gelation technique) has been exploited to prepare multiparticulate systems, incorporating numerous drugs, proteins, cells or enzymes. Alginates are polysaccharides derived mainly from brown seaweed. Sodium alginate is the water soluble form, that upon quenching with Ca^{2+} crosslinks to the water insoluble form of calcium alginate. The divalent cation bridges the gap between two polymer chains, in turn stabilizing the network. This material, calcium alginate, is biocompatible, biodegradable, immunogenic, non-toxic, economical and can be easily prepared [26]. Alginate beads face problems such as distorted shapes, uneven sizes, poor mechanical strength and high porosity [27]. To improve the

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properties of the beads, alginate can be loaded with montmorillonite clay [28]. Montmorillonite is a layered structure consisting of a sandwich of one octahedral alumina sheet between two tetrahedral silica sheets [29]. Fortunately, this clay not only improves the mechanical properties of the beads, but also the adsorptive properties. The montmorillonite (natural or modified) has been used for more than 40 years for the removal of toxic metals or organic pollutants [30–33] from aqueous solutions. This inorganic solid has favourable surface properties, availability, environmental and economic considerations. The specific properties of montmorillonite are its high cation exchange capacity, adsorption, high surface area and swelling behaviour [34].

In recent years, clays supported on calcium alginate beads have been reported to improve the mechanical and thermal stabilities of the beads and also to simplify the separation procedures compared to the use of natural clays [35]. The most interest in studies for the use of alginate-clays beads as adsorbents has been for the removal of dyes from aqueous solutions [36–38] or for controlled release of difference substances [39,40]. However, there are insufficient studies for the use of these kinds of materials to adsorb pesticides for cleaning or decontamination. In the particular case of PQ, montmorillonite has been used in several reports as the adsorbent [41,42], but there is not information regarding alginate-montmorillonite beads as adsorbent of PQ. Besides, it is unknown if the montmorillonite forming the bead adsorbs PQ in the same way that the montmorillonite in powder does. The possibility to use these beads instead of the powdered clay to remove pesticides would really be a significant improvement of remediation technologies using adsorption process. The use of these materials would help during the separation process because it is not necessary to wait a long time for sedimentation after adsorption, as it occurs with clays [43]. Centrifugation will not be necessary either because after shaking and due to gravity, the alginate-montmorillonite beads are deposited at the bottom of the reactor.

In this report we present the synthesis and characterization of alginate beads with different contents of montmorillonite. The aim is to study the adsorption of PQ onto these alginate-montmorillonite beads from aqueous solutions and to assess how the clay content affects the adsorption. The role played by alginate and montmorillonite in the beads is investigated and highlighted.

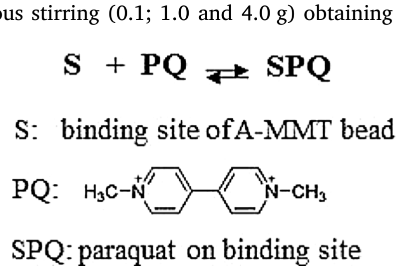
2. Experimental

2.1. Materials and reagents

Sodium alginate was obtained from Fluka (Switzerland, N° 71238), Mw = 231,500 g/mol) Na-Montmorillonite (99.4% purity) was obtained from Lago Pellegrini (Rio Negro, Argentina). Paraquat (99%) was supplied by Supelco (molecular structure shown in Scheme 1) and calcium chloride ($CaCl_2$) was supplied by Sigma-Aldrich Company.

2.2. Synthesis and characterization of alginate-montmorillonite beads

A 1% (w/v) Na-alginate solution was prepared by solving 1 g of sodium alginate into 100 mL distilled water at room temperature. Then, different amounts of montmorillonite (MMT) were added to the gel with continuous stirring (0.1; 1.0 and 4.0 g) obtaining suspensions of



Scheme 1. Describes in a general way the adsorption reaction of PQ onto A-MMT beads.

Table 1
Sample description.

Alginate suspension (%)	MMT suspension (%)	MMT content per gram of bead (%)[a]	Denomination
1	0	0	**A-MMT0**
1	0.1	5	**A-MMT5**
1	1	30	**A-MMT30**
1	4	70	**A-MMT70**

[a] The MMT content per gram of bead was estimated from elemental analysis shown in Section 3.1.

0.1; 1 and 4% (w/v) of MMT. Once the mixture was homogeneous it was forced through a micropipette tip by a peristaltic pump. The resulting gel droplets were collected in a stirred reservoir containing 0.1 M $CaCl_2$ solution. The beads were allowed to harden in this solution for few minutes. Afterwards hard spherical beads containing the MMT were obtained. The beads were filtered and rinsed several times with distilled water to remove calcium chloride from its surface. They were then stored in NaCl 0.1 M until use. When calcium alginate beads were used as a blank, the same procedure as before was followed, but in this case there was no addition of MMT.

The beads will be named as **A-MMT0**; **A-MMT5**; **A-MMT30** and **A-MMT70** as is shown in Table 1.

2.3. Characterization

Exeter Analytical, INC, model CE440 Elemental Analysis instrument was employed in the performance of the elemental analysis of the alginate and alginate-montmorillonite beads. The wet beads were observed with a D5100 Nikon Digital camera. The shape, external morphology and internal structure of the beads were examined by scanning electron microscopy (SEM). Images (at different magnifications) of dry whole beads and their cross sections were captured on an LEO microscope model EVO 40. The samples were exposed to an accelerated voltage beam strength of 10.0 KV.

The thermogravimetric analysis (TGA) was performed with the STD Q600 of TA Instruments operated in air. The 25 μg powder samples in a ceramic crucible were heated in air from 20 °C to 1000 °C at the rate 10 °C/min. The maximum variability between two replicates was 0.2% on a mass basis. The maximum degradation temperature was determined with a precision of ± 3 °C.

The crystallinity and structure of the dried materials were examined by XRD on a Rigaku D-Max III – C equipped with a Cu $K_{\alpha 1}$ (λ = 1.54059 Å) radiation and graphite monochromator operated at 35 kV and 15 mA over the 2θ range of 3–80° and 25 °C at a scan rate of 0.02° s^{-1}. The XRD patterns are presented in the Supplementary material.

The FTIR spectra of the samples were recorded using KBr pellets on a Nicolet Nexus 470 FTIR spectrometer equipped with a DTGS detector over a range of 4000–400 cm^{-1}.

The N_2 adsorption-desorption isotherms at 77 K (BET) were performed with a Micromeritics – ASAP 2000 instrument. Prior to the measurements, the dried samples were outgassed for at least 12 h at 333 K.

Electrophoretic mobilities of sodium alginate, MMT, A-MMT0, A-MMT70 and A-MMT70 with PQ adsorbed (PQ_{ads} A-MMT70) at different pH and in 0.01 M NaCl were determined with a Malvern Nano ZS90 equipment. The experiments were carried out at 25.0 °C. Zeta potential (ζ) data were automatically calculated with the Smoluchowski equation by the equipment. It was necessary to dry the beads, grain them and prepare the suspensions in 0.01 M NaCl. Although this preparation changed the appearance of the beads, the information obtained was useful. The concentration of the solid was 0.1 g L^{-1} for MMT, A-MMT0, A-MMT70 and PQ_{ads} A-MMT70 and 1 g L^{-1} for sodium alginate.