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Research paper

## Removal of anionic and cationic dyes from aqueous solution with activated organo-bentonite/sodium alginate encapsulated beads

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## ABSTRACT

In this study, cross-linked activated organo-bentonite (AOBent)/sodium alginate (SA) composite was prepared by the intercalation of sodium alginate in activated organo-bentonite and the cross-linking reaction between sodium alginate and chlorhydric acid to produce interesting new low cost material for the removal of cationic and anionic dyes (methylene blue (MB) and methyl orange (MO)) from aqueous solutions. Adsorbents were characterized by using X-ray diffraction (XRD), thermal gravimetric analyses (TGA) and Fourier transform infrared spectroscopy (FTIR). Batch adsorption studies were carried out to evaluate the effect of pH solution, the kinetic and the isotherm on the adsorption capacity of the adsorbents. The kinetic of MB and MO adsorption was found to follow a pseudo-second-order kinetic model meanwhile the isotherm was well described by the Langmuir model for all samples. Results obtained from this study suggest the potential of prepared composites for cationic and anionic dyes removal which can also be used easily for clean and ecofriendly processes.

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## 1. Introduction

Dyes have polluted waterways from rapidly growing industrial activities. The polluted water becomes a danger to the public since the dyes can inflict life-threatening diseases and also devalue the aesthetic nature of the water bodies, leading to abnormal variations in the aquatic environment (Oladipo and Gazi, 2014). Even at minimum concentrations, dyes may be toxic and difficult to decolorize due to their complex structure (Crini and Badot, 2008). Several methods of wastewater treatment such as advanced oxidation process (Sakkas et al., 2010), aerobic or anaerobic digestion (Kokabian et al., 2013) and coagulation (Lau et al., 2014) have been applied for the removal of dyestuff from aqueous solutions. However, most of these procedures show low effectiveness, high cost and/or undesirable environmental impact (Luo et al., 2010). Thus, there is a need to develop new effective decolorization and decontamination methods. In particular, adsorption methodologies, utilizing biological materials, mineral oxides, activated carbons, or polymer resins, have been proposed in the last years (Mohan and Pittman, 2007). A large variety of non-conventional adsorbents materials have been proposed and studied for their ability to remove dyes (Crini, 2006). To be industrially acceptable, the adsorbents must be efficient and eco-friendly but also abundantly available. Clays comply with

most of these features and have been applied in various fields of adsorption science (Oladipo and Gazi, 2014). The great interest in natural or modified clays as adsorbents materials is mainly related to the large specific areas associated with their layered structure, the ease with which they are obtained or modified, and the possibility of modifying their surfaces to increase their affinity for specific adsorbates (Lezeshari et al., 2010). In particular, some Algerian bentonites have been proposed to be used in drilling of oil wells (Didi et al., 2009), in sorption of metals (Ararema et al., 2011), herbicides (Ait Sidhoum et al., 2013), catalysis (Ali-dahmane et al., 2014) and sorption of dyes (Benhouria et al., 2015). Surface modifications of these natural bentonites by exchanging interlayer inorganic cations (e.g. Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>) with organic cations, such as quaternary alkylammonium, result in modified bentonites with improved properties (Zaghouane-Boudiaf and Boutahala, 2011a). Together, acid treatment of these natural Algerian bentonites at high temperature have been used to improve the adsorption properties by increasing the number of active sites, surface area and porosity (Min-Yu and Su-Hsia, 2006). The obtained modified and/or activated bentonites highly increase their adsorption capacities toward organic compounds and cationic species (Komadel and Madejová, 2006). Nevertheless, recovering and regeneration of these clay-based adsorbent from solution may result difficult due to their colloidal dimensions, weakening their industrial use. Encapsulation of clay particles into a polymer matrix composed of naturally occurring polysaccharides appears as an effective alternative to obtain low cost composite beads with adequate dimensions and effective sorption capacities (Viseras et

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al., 2008; Bergaya and Lagaly, 2013). The degree of interaction between the clay particles and polymer chains greatly depend on the nature and properties of the components but also on the methodology used to prepare the nanocomposites, resulting in different structures that may be classified according to the level of intercalation of polymer chains into the clay structure and resultant clay layer exfoliation (Alexander and Dubois, 2000; Mondal, 2013). Alginate, a natural polysaccharide produced by brown algae and bacteria and composed of linear binary copolymers of  $\beta$ -D-mannuronic acid and  $\alpha$ -L-guluronic acid (Govan et al., 1981) have been considered in the removal of pollutants (Annadura et al., 2002; Aravindhana et al., 2007 (a)) and adsorption of active pharmaceutical ingredients and biological substances (enzymes, microorganisms, animal or human cells) (Zaghoulane-Boudiaf and Boutahala, 2011a). Alginate have been also proposed in the development of clay/alginate nanocomposites (Wang et al., 2013; Barreca et al., 2014).

With these premises, aim of this work was to prepare a low cost pollutant adsorbent composed of sodium alginate and activated organo-bentonite. The polymer was intercalated into the clay layers at different ratios and cross-linked beads were obtained in an inverse dispersion system by addition of calcium chloride. The structure and morphology of the resultant beads were studied with XRD, TGA and FTIR and the adsorption properties were investigated with two model pollutants: methylene blue (MB) and methyl orange (MO) respectively as cationic and anionic dyes. As others dyes MB and MO are toxic substances but have a widespread use and high stability and they are very resistant to biological degradation so it is urgent to removal there from water.

## 2. Material and methods

### 2.1. Materials

A natural bentonite (Bent) supplied by the National Company of Useful Substances and Products Non Ferrous, Algeria was grinded and sieved ( $<125\ \mu\text{m}$ ). Its mineralogical and chemical composition has been studied previously ( $\text{SiO}_2$ , 56.85%;  $\text{Al}_2\text{O}_3$ , 18.57%;  $\text{Fe}_2\text{O}_3$ , 2.92%;  $\text{TiO}_2$ , 0.19% (wt.%)), as well as the cation exchange capacity (0.90 meq/g) and specific surface area ( $80\ \text{m}^2/\text{g}$ ) (Zaghoulane-Boudiaf and Boutahala, 2011b; Arbaoui and Boucherit, 2014). Hexadecyltrimethylammonium bromide, sulfuric acid, calcium chloride, methyl orange ( $\text{C}_{14}\text{H}_{14}\text{N}_3\text{NaO}_3\text{S}$ , abbreviated as MO) and methylene blue ( $\text{C}_{16}\text{H}_{18}\text{N}_3\text{S}$  abbreviated as MB) were acquired from Sigma–Aldrich Chemicals and used as received without further purification. Sodium alginate (SA) was purchased from R&M Chemicals.

### 2.2. Preparation of activated organo-bentonite/sodium alginate beads

Activated organo-bentonite (AOBent) was synthesized according to a previous methods (Zaghoulane-Boudiaf and Boutahala, 2011a; Zaghoulane-Boudiaf et al., 2014) starting by activation using acid treatment of bentonite to obtain activated bentonite (ABent) which organophilised later to obtain activated organo-bentonite (AOBent). Sodium alginate water solution (2% w/v) was prepared with stirring for 1 h and then 2, 4 and 6 g of AOBent powder was added into the solution under stirring overnight to obtain homogeneously dispersed alginate–AOBent dispersion.

The result was dropped through a burette into a precipitation bath containing 4% (w/v) calcium chloride solution under vigorous stirring to form beads. The composite beads were washed several times with deionized water until the excess unbounded calcium chloride was removed then dried for 48 h at room temperature. The weight ratio between sodium alginate and AOBent was 1:1, 1:2, 1:3 which was referred to AOBent/SA 1/1, AOBent/SA 2/1 and AOBent/SA 3/1 respectively. To compare, SA beads in absence of AOBent were also prepared. Briefly, a sodium alginate water solution (2% w/v) was dropped through a burette into a 4% (w/v) calcium chloride water solution under vigorous stirring to form beads. The resultant beads were allowed to stand for 10 h to ensure a complete gelation and then excess unbounded calcium chloride was removed by washing with deionized water until neutral pH attached. The washed beads were dried for 48 h at room temperature. The typical pictures of the capsules prepared in this study were shown in Fig. 1. Spherical capsules with an external diameter of about 1 mm were found for SA and AOBent/SA 3/1. The introduction of AOBent into SA capsules was confirmed from the colour of the capsules (Fig. 1(B)).

### 2.3. Characterization of adsorbents

X-Ray powder diffraction (XRPD) was done by using a Philips® X-Pert diffractometer with  $\text{Cu K}\alpha$  radiation. The diffraction data were analysed using the XPOWDER® software (Martín-Ramos, 2004).

Thermogravimetric analysis (TGA) was carried out using a METTLER TOLEDO mod. TGA/DSC1 with FRS5 sensor and a microbalance (precision  $0.1\ \mu\text{g}$ ) (Mettler-Toledo GMBH). Samples were heated under nitrogen atmosphere in the interval  $30\text{--}400\ ^\circ\text{C}$  at  $10\ ^\circ\text{C}/\text{min}$ . Fourier transform infrared spectroscopy (FTIR) analysis of the adsorbent was carried out in KBr pellets in the range of  $4000\text{--}400\ \text{cm}^{-1}$  with using FTIR 8400S Shimadzu having a standard mid-IR DTGS detector.

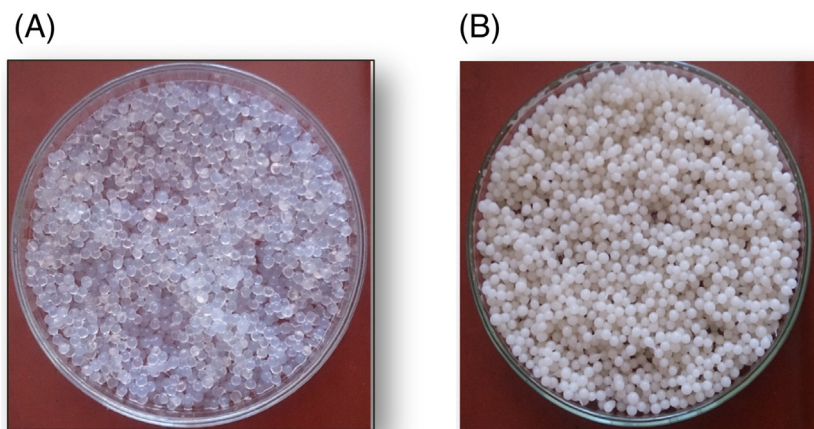


Fig. 1. Beads photos (A) dry SA, dry AOB/SA 3/1.

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