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Sorption of chrysoidine by row cork and cork entrapped in calcium alginate beads

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Abstract Azo-dyes, molecules characterised by the presence of the azo-group (–N═N–), are widely used in textile, leather, rubber, plastic, and food industries. Water-soluble azo-dyes are greatly resistant to biodegradation, and are characterised by a high thermal and photo stability due to their complex structures. The release of these molecules into the environment is of crucial concern due to their toxic, mutagenic and carcinogenic characteristics. Biosorption has been demonstrated an effective method to remove pollutants from wastewaters thus solving ecological tasks, being a low cost process and the sorbent biodegradable. The main requirements of an efficient sorbent are thermal, chemical and mechanical stability, and rapid sorption.

In this work, the ability of both row cork and the same sorbent entrapped in a biopolymeric gel of calcium alginate, on the removal of chrysoidine from aqueous solutions was examined.

The influence on the sorption of pH, initial dye concentration, and particle size, as well as the efficiency of the entrapment, have been investigated. The maximum sorption was found for cork samples of fine particle size (FC), in both row and entrapped forms, at pH 7; conversely, at pH 4 the difference is significant (0.12 mmol/g for row cork and 0.20 mmol/g for entrapped cork), evoking a cooperation of alginate in binding the positively charged chrysoidine molecule.

1. Introduction

Among the various techniques for removal of pollutants from waste waters (chemical precipitation and filtration, biodegradation, electro-chemical treatments, chemical coagulation, reverse osmosis, ion exchange, oxidation and adsorption), sorption of both metal ions and organic molecules from waters by biomass has been found to be an effective removal method, due to its efficiency, simplicity, easy applicability, and

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cost-effectiveness (Guiso et al., 2012; Nurchi and Villaescusa, 2012). Cork, thanks to the different chelating groups on its surface, behaves as a strong sorbent towards most of the polluting metal ions (Villaescusa et al., 2002) and it presents good perspectives for organic contaminants (Nurchi et al., 2010, 2008; Nurchi and Villaescusa, 2008).

Azo-dyes, molecules characterised by the presence of the azo-group (–N═N–), are widely used in the textile, leather, rubber, plastic, and food industries (Erkurt, 2010). Water-soluble azo-dyes are greatly resistant to biodegradation, and are characterised by a high thermal and photo stability due to their complex structures. Large volumes of coloured effluents are discharged into receiving waters: the coloured wastewater may to some extent inhibit vital photosynthetic processes, and, furthermore, produces an unpleasant environmental impact. The release of these molecules into the environment is of crucial concern due to their toxic, mutagenic and carcinogenic characteristics. Toxic effluents containing azo-dyes are discharged from various industries and they pose toxicity (genotoxicity, mutagenicity, carcinogenicity with often lethal effects) to aquatic organisms (bacteria, algae, fish, . . .) and animals (Puvaneswari et al., 2006). Thus, the removal of azo-dyes from wastewaters is a fundamental environmental issue.

Chrysoidine is a synthetic azo-dye widely used in the textile industry. It undergoes reduction followed by a chain of reactions leading to the formation of toxic compounds. Oral administration of chrysoidine results in liver-cell adenomas, carcinomas and leukaemia in animals, and some case studies suggest its carcinogenicity as well (Lei et al., 2011). Various researchers have studied the adsorption of this dye on different materials. Activated carbon has been found to be effective, having both high surface area and high sorption capacity. However, its relatively high operation costs hamper its large-scale application. Therefore, a number of low-cost sorbents have been examined for dye removal (Ho and McKay, 1998; Matheswaran and Karunanithi, 2007; Mittal et al., 2010; Purkait et al., 2004). It is also recognised that, in order to facilitate sorbent application, the raw material can be entrapped in calcium alginate gel matrix. Alginates are salts of unbranched copolymers of β-D-mannuronic and α-L-guluronic acids extracted mainly from brown seaweed. By association with most divalent cations, such as calcium, they produce thermally irreversible gels. Calcium alginate was used as an encapsulating polymeric matrix due to its low-cost, biodegradability, high and easy encapsulation capability. This kind of encapsulating procedure was successfully applied for the entrapment of grape stalk waste from wine production and solid by-products from electroplating and metal surface treatment industries (Garlaschelli et al., 2013).

In the present work, cork has been investigated as sorbent for Chrysoidine G (Fig. 1).

The comparison among the maximum sorption capacity of row cork samples at two different particle sizes (labelled as FC and GC with nominal diameter over 40 mesh and between 20–40 mesh, respectively) and the finest cork fraction (FC) entrapped in calcium alginate gel beads has been examined at 25 °C and at two different pH. In particular pH 4 and 7 are chosen to study the effect of the surface charge of the solid phase on the dye sorption.

A spectrophotometric study of the protonation properties of Chrysoidine G is furthermore presented to elucidate the sorption mechanism of the dye on the biosorbent.

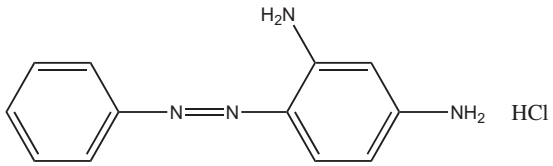

Figure 1 Chemical structure of Chrysoidine G.

2. Experimental

2.1. Materials

All the reagents (Chrysoidine G, calcium alginate, $CaCl_2$, KOH, KCl and HCl), purchased from Aldrich (analytical grade), were used without further purification. Chrysoidine G (1,3-benzenediamine, 4-(phenylazo)-monohydrochloride M.W. 248.72) is highly soluble in water. A stock solution of Chrysoidine G was prepared by dissolving the proper amount in double distilled water. Cork was kindly supplied by cork taps manufacturer from Cassà de la Selva, Girona (Spain). Cork samples of two different sizes were selected according to the Tyler mesh size (Particle Size – US Sieve Series and Tyler Mesh Size Equivalents, 2009) and labelled as FC and GC (nominal diameter over 40 Mesh and between 20–40 Mesh, respectively). Cork particles, rinsed three times with boiling water and three times with distilled water, were dried in a vacuum oven at 60 °C, then stored in a desiccator at room temperature. Alginate beads containing 2% (w/v) FC particles entrapped into a calcium alginate gel were obtained, following the procedure previously reported by Fiol et al. (2004, 2005). Sodium alginate salt was used as the gelling material, with 0.1 M $CaCl_2$ as fixing solution.

2.2. Chrysoidine G chemical characterisation

Protonation equilibrium of Chrysoidine G was studied by spectrophotometric titration. The experiments were performed in a thermostated glass cell equipped with a magnetic stirrer, a glass electrode (Metrohm LL UNITRODE), connected to a pH-metre (Metrohm 691), an inlet–outlet tube for Argon and a fibre optic dip probe connected to a Varian Cary 50 UV–vis spectrophotometer. The accuracy and precision of this equipment were previously determined by Crisponi et al. (2004). The potentiometric cell was standardised in the H^+ concentration employing alkalinimetric titrations of HCl with KOH, at ionic strength 0.1 M KCl, and the results were analysed with Gran procedure (Gran, 1952). The protonation equilibrium has been studied on 15 solutions of 0.1 M KCl, at different pH (ranging from 3 to 8) containing Chrysoidine G 5.6×10^{-5} M. The pH of each solution was adjusted by adding small amounts of HCl 0.01 M or KOH 0.01 M and it is measured with the above described calibrated cell. The spectrum of each solution was recorded in the 300–600 nm spectral range with 1 cm path length and the data were processed by Hyperquad program (Gans et al., 1996).

2.3. Sorption isotherm procedure

Sorption isotherms are widely used to characterise retention of chemicals in solid phase. In our experiments, a fixed amount