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Natural waste materials containing chitin as adsorbents for textile dyestuffs: Batch and continuous studies

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Abstract

In this work three natural waste materials containing chitin were used as adsorbents for textile dyestuffs, namely the Anodonta (*Anodonta cygnea*) shell, the Sepia (*Sepia officinalis*) and the Squid (*Loligo vulgaris*) pens. The selected dyestuffs were the Cibacron green T3G-E (CI reactive green 12), and the Solophenyl green BLE 155% (CI direct green 26), both from CIBA, commonly used in cellulosic fibres dyeing, the most used fibres in the textile industry.

Batch equilibrium studies showed that the materials' adsorption capacities increase after a simple and inexpensive chemical treatment, which increases their porosity and chitin relative content. Kinetic studies suggested the existence of a high internal resistance in both systems. Fixed bed column experiments performed showed an improvement in adsorbents' behaviour after chemical treatment. However, in the column experiments, the biodegradation was the main mechanism of dyestuff removal, allowing the materials' bioregeneration. The adsorption was strongly reduced by the pore clogging effect of the biomass.

The deproteinised Squid pen (grain size 0.500–1.41 mm) is the adsorbent with highest adsorption capacity (0.27 and 0.037 g/g, respectively, for the reactive and direct dyestuffs, at 20 °C), followed by the demineralised Sepia pen and Anodonta shell, behaving like pure chitin in all experiments, but showing inferior performances than the granular activated carbon tested in the column experiments.

Keywords: Adsorption; Activated carbon; Chitin; Dyestuffs; Low-cost adsorbents; Textile wastewaters

1. Introduction

The textile industry uses large volumes of water in wet processing operations and, thereby, generates substantial quantities of wastewater containing large amounts of dissolved dyestuffs and other products, such as dispersing agents, dyebath carriers, salts, emulsifiers, levelling agents and heavy metals (Reife and Freeman, 1996).

It is nowadays well known the need of treating textile wastewaters, not only concerning primary and secondary treatments for organic matter and suspended solids removal, but also a tertiary treatment, mostly for residual colour removal.

The textile industry is always looking for persistent and bright colours, in order to please the consumers. So, the

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Nomenclature

A_t	specific surface area (m^2/g)
C	dyestuff concentration of the liquid phase in the adsorber (g/L)
CE	inlet dyestuff concentration of the liquid phase in the adsorber (g/L)
d_{max}	maximum dimension of the dyestuff molecule (nm)
$d_{particle}$	average particle diameter (μm)
d_{pores}	average pore size diameter (nm)
GAC	granular activated carbon
k_f	film mass transfer coefficient (cm/s)
k_L	Langmuir equation constant (cm^3/g)
MW	molecular weight
N_d	number of internal mass transfer units
N_f	number of film mass transfer units
Ni Pc	nickel phthalocyanine
Pe	axial Peclet number
PE	polyethylene
q	dyestuff concentration in the adsorbent (g/L)
q_s	adsorbent maximum capacity (g/g)
r	correlation coefficient
TC	total carbon (mg C/L)
TIC	total inorganic carbon (mg C/L)
TOC	total organic carbon (mg C/L)
TSS	total suspended solids (mg/L)
ε_p	particle porosity (cm^3 fluid /cm^3 particle)
λ_{max}	wavelength of maximum absorbance (nm)
θ	time normalised by the mean residence time in the adsorber
ρ_{ap}	apparent density (g/cm^3)
σ^2	variance
ξ	adsorber capacity factor

dyestuffs are becoming progressively more and more resistant to the traditional processes of treating wastewater.

This explains the appearance of the youngest and most important class of dyestuffs, the reactive dyestuffs. They offer bright and long lasting colours to the dyed material, because they bind themselves to the fibres, but they lead to poor exhaustion levels in the dyeing bath, when compared with other classes of dyestuffs. This results in a large amount of these dyestuffs going everyday to the wastewaters, and their resistant molecules make the effluents difficult to treat.

The biological treatments, as the activated sludge and trickling filter processes, often used for organic matter removal, have been decreasing their efficiency in colour removal, through the last decades, with the appearance of new dyestuffs, more resistant to biodegradation. The coagulation/flocculation technique was traditionally used for colour removal, but the inorganic salts used for coagulation became inefficient for the removal of reactive dyestuffs and generate large amounts of sludge. New coagulants, organic polymers which could remove these dyestuffs were developed. They generate smaller amounts of sludge, however some of them (cationic polymers) seem to be more toxic to the aquatic environment than most of the dyestuffs.

One of the most used processes for colour removal has been adsorption with activated carbon, an efficient solution. However, this treatment needs a high investment and operating costs, due to the high price of the activated carbon and to the high wastewater flowrate always involved, and these costs can be greatly increased when there are no carbon regeneration units locally, as in the case of Portugal.

Research has recently been directed towards alternative adsorbents, namely low-cost adsorbents, including the utilisation of natural and waste materials. Many research works studying valuable alternatives to activated carbon for dyestuffs removal appeared, using: inorganic adsorbents such as bentonite, fly ashes and steel plant slag (Ramakrishna and Viraraghavan, 1997), natural zeolites (Meshko et al., 2001) and dolomite (Walker et al., 2003); synthetic polymers derived from cellulose (Hwang and Chen, 1993a, b; Abo-Shosha et al., 1993); natural adsorbents from vegetal source like Eucalyptus bark (Morais et al., 1999) and modified peat-resin particles (Sun and Yang, 2003), and from animal sources, like chitin (poli-(1→4)-*β*-*N*-acetil-D-glucosamine) and chitosan (poli-(1→4)-*β*-D-glucosamine) (Koonce, 1993; McKay, 1996).

The use of chitin and chitosan (deacetilated chitin) showed promising results. The study of these biopolymers led to the production of fibres, which are better than activated carbon fibres both in removal efficiencies and in the recovery of the acid and direct dyestuffs (Yoshida et al., 1991, 1992), and crosslinked fibres with improved strength (Wei et al., 1992). They attracted much interest because of their biodegradability, wound-healing acceleration capability and many other unique properties. As a natural renewable resource, they offer many potential applications in a number of diversified fields (Agboh and Qin, 1997).

Three natural waste materials from the Portuguese seafood industry were used in this work: the Anodonta (*Anodonta cygnea*) shell, the Sepia (*Sepia officinalis*) and the Squid (*Loligo vulgaris*) pens. They are composed of minerals, proteins and chitin. They were studied as potential alternatives to granular activated carbon and compared with pure chitin, before and after chemical treatment—a simple and non-expensive treatment of mineral/protein removal, according to the material.