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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.
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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.

The selected dyestuffs were the CI reactive green 12, Cibacron green T3G-E—which belongs to the most used class of dyestuffs and also the most difficult to remove from wastewaters by the traditional processes—and the CI direct green 26, Solophenyl green BLE 155%, both from CIBA. The reactive and direct dyestuffs are commonly used in the dyeing of cellulosic fibres, the most used in the textile industry.

2. Materials and methods

2.1. Dyestuff preparation

Solutions of the direct dyestuff Solophenyl green BLE 155% (CI direct green 26) and of the reactive dyestuff Cibacron green T3G-E (CI reactive green 12), both from CIBA (Basel, Switzerland), were prepared with distilled water in concentrations of 50 and 180 mg/L, respectively, which are within the typical concentration range found in textile wastewaters.

In order to work with the dyestuffs in the same form as they are found in wastewaters, their preparation follow the typical procedures used in the textile dyeing industry. The direct dyestuff solution was obtained after a 30-min boiling period to reach complete dissolution. The reactive dyestuff solution was boiled for 20 min before the addition of 2 g/L of sodium hydroxide and boiled for more 20 min to reach its hydrolysis and then neutralised with sulphuric acid (Figueiredo et al., 1998a, b).

Some general characteristics and the chemical structure of both dyestuffs are shown respectively, in Tables 1 and 2. It is important to remind the high molecular weight and maximum dimension of both dyestuffs that will cause difficulties to the molecules' migration through the adsorbent pores.

2.2. Adsorbents preparation

The adsorbent materials, Anodonta (*A. cygnea*) shells, Sepia (*S. officinalis*) and Squid (*L. vulgaris*) pens, are wastes from the Portuguese seafood industry. They were only washed with tap water, dried at 40 °C, ground and sieved.

All experiments in this work were performed with particles of grain size between 0.500 and 1.41 mm, i.e., 32–12 Tyler mesh.

In order to improve the performances of these natural materials as adsorbents, they were also chemically treated. Since they are composed of minerals, mostly crystalline calcium carbonate, proteins and chitin, they are often submitted to demineralisation and/or deproteinisation processes (Kurita et al., 1993; Koonce, 1993).

Previous studies (Figueiredo et al., 1998b) show that for the materials with higher mineral content, Anodonta shells and Sepia pens, the demineralisation treatment is the most suited. For the Squid pens, a material with a higher content in proteins than in minerals, the deproteinisation treatment seems advantageous.

The demineralised materials were obtained after reaction with 10% HCl (15 mL/g material) at room temperature, until neutral (or constant) pH was reached. The deproteinisation was performed at 75–80 °C, using 10% NaOH (15 mL/g material), during 6 h. After the chemical treatments the materials were filtered over a PE filter, washed with distilled water and acetone, and finally dried at 40 °C and sieved (Figueiredo et al., 1998b).

The chemical treatments remove almost completely the minerals or proteins, and the materials become almost pure chitin. The chitin content was initially less than 5% in the Anodonta shells and Sepia pens, and around 40% in the Squid pen (Goffinet and Jeuniaux, 1979; Knorr, 1984; Machado et al., 1991). The chitin enrichment was accompanied by an increase in the pore size diameter and porosity. More details about these treatments can be found elsewhere (Figueiredo, 2002).

The main physical properties of the materials before and after chemical treatment, determined by mercury porosimetry are presented in Table 3, i.e., the average particle diameter ($d_{particle}$), the specific surface area (A_t), the average pore size diameter (d_{pores}), the particle porosity (ε_p) and the apparent density (ρ_{ap}) (Figueiredo et al., 2000). It can be observed the low specific surface areas of the natural materials, when compared with traditional adsorbents. In the Anodonta shell the macropores are dominant (> 50 nm); in the Sepia pen although smaller pores exist there is also a predomination of macropores; in the Squid pen the pore size distribution is bimodal with predominating mesopores (2–50 nm). Albeit the existence of micropores (< 2 nm) in these materials, their volumes were not determined (they are below the detection limit of mercury porosimetry) because the dyestuff molecules cannot penetrate them due to their dimensions (estimated 2 and 4 nm,

Table 1
Dyestuffs' general characteristics

Generic name	Chemical class	Molecular formula	MW	d_{max} (nm)	λ_{max} (nm)
CI direct green 26	Triazo	$C_{50}H_{38}N_{12}O_{18}S_4.5Na$	1338.1	2	620
CI reactive green 12	Phthalocyanine	$C_{60}H_{29}Cl_3N_{16}NiO_{21}S_7.6Na$	1837.7	4	345

Table 2
Dyestuffs' chemical structure

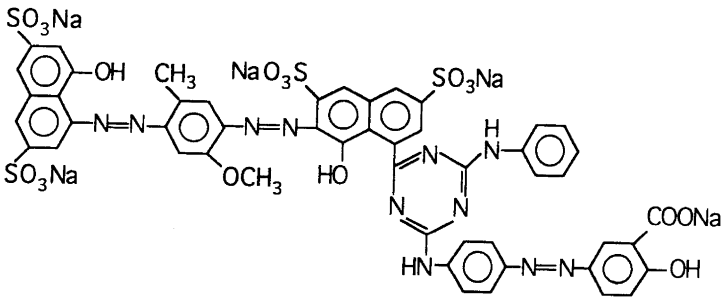
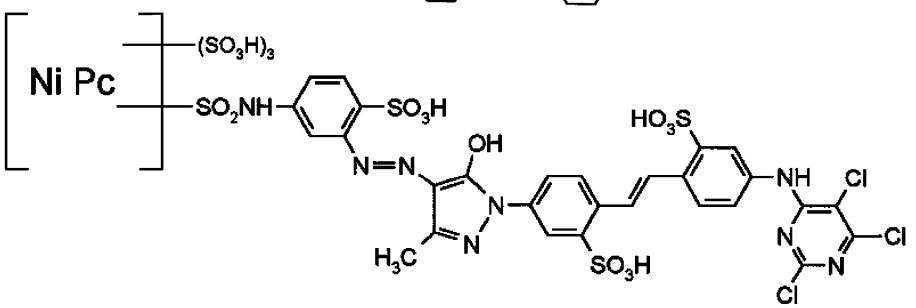
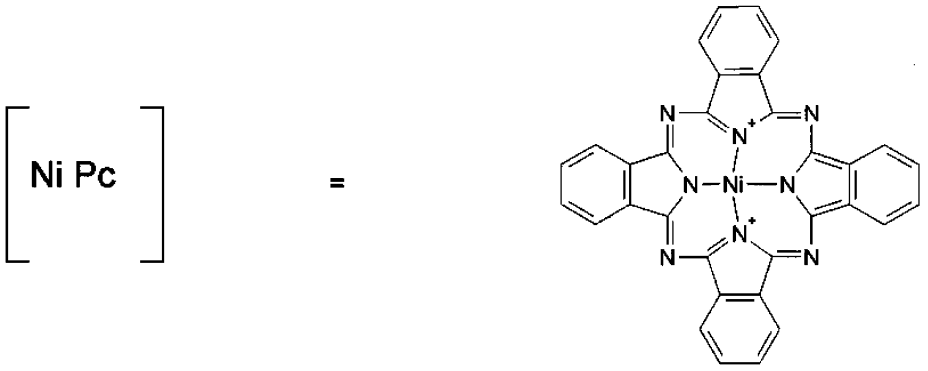
Generic name	Chemical structure
CI direct green 26	
CI reactive green 12 (free acid form)	
	

Table 3
The materials' physical properties (grain size between 0,500 and 1,41 mm) before and after chemical treatment

Adsorbent	Treatment	$d_{particle}$ (μm)	A_t(m^2/g)	d_{pores} (nm)	ε_p (%)	ρ_{ap} (g/cm^3)
Anodonta shell	None	1003	1.42	78.1	7.4	2.666
	Demineralisation	1240	4.57	190	31.4	1.446
Sepia pen	None	1157	4.11	71.8	16.3	2.211
	Demineralisation	1585	7.61	127	27.7	1.148
Squid pen	None	1768	8.82	45.7	12.9	1.281
	Deproteinisation	1159	12.16	88.8	30.1	1.116
Chitin	—	1318	15.2	101	38.3	1.004

respectively, for the direct and reactive dyestuffs, using the software CHEM-X that calculates the relative position of the atoms based on the minimisation of the mechanical energy of the molecule in vacuum).

Chitin practical grade from crab shells from Sigma Chemical Co. (St. Louis, MO, USA) and the granular activated carbon Sutcliffe GAC 10-30 from Sutcliffe Speakman Carbons (Lancashire, UK) were also used in order to compare their performances with the selected materials. The chitin physical properties can be found also in Table 3. The commercial granular activated carbon used presented a particle average diameter of 1134 μm and a specific surface area around 900–1000 m^2/g.

2.3. Equilibrium batch studies

Equilibrium adsorption isotherms were determined in a refrigerated incubator P-Selecta Hotcold-M (Barcelona, Spain), with an orbital P-Selecta Rotabit shaker (Barcelona, Spain) using a stirring speed of 100 rpm, at 20 °C. A set of 100 mL erlenmeyers with 50 mL of dyestuff solution and different amounts of the same adsorbent were shaken during 15 days—time enough to reach the adsorption equilibrium in the systems studied. In each experiment the air in the adsorbent pores was previously removed by a vacuum pump when the adsorbent was immersed in distilled water, to allow a full contact adsorbent/adsorbate.

For each dyestuff solution a blank test was run, in the same conditions. At the end, after 30 min centrifugation in a centrifuge mLw T54 (Leipzig, Germany), the dyestuff concentration was measured using a UV/VIS PYE UNICAM PU 8600 spectrophotometer from Philips (Cambrige, UK) at a wavelength corresponding to the dyestuff maximum absorbance and the pH was measured with a pH meter WTW pH90 (Weilheim, Germany).

2.4. Desorption and regeneration experiments

The saturated materials obtained after the column experiments, described below, were used in desorption and regeneration experiments. The dyestuffs desorption was evaluated after an 11-days contact time with distilled water, at 20 °C. The regeneration experiments were performed in the same way for the systems that have shown the highest adsorption capacities, but using diluted sulphuric acid and sodium hydroxide solutions. Regeneration at high temperature (79 °C) was also evaluated after a 2 h period of continuous magnetic stirring at 500 rpm.

2.5. Evaluation of leaching

The natural materials were contacted with distilled water during 15 days (the same period that was used in the equilibrium experiments), at 20 °C, in order to evaluate possible leaching of their main components. The smallest grain size fraction obtained after grinding (less than 0.063 mm) was used to facilitate the migration to the solution. All determinations were preceded by filtration using a filter Whatman GF/C (Maidstone, UK) to eliminate interferences due to the presence of suspended solids and turbidity. The main components analysed and the methods of analysis are presented in Table 4. A TC/TIC/TOC analyser Dohrmann DC 190, Rosemount Analytical (Santa Clara, CA, USA) and an atomic absorption spectrophotometer GBC 902 (Melbourne, Australia) were used.

2.6. Continuous stirred tank adsorber studies

Kinetic studies were performed in a cylindrical acrylic Carberry-type adsorber, with 12.3 cm height and 11 cm inside diameter, with four baskets, in opposite positions. Each one was filled with the same amount of weighted adsorbent, preventing this way the mechanical attrition of the particles. An adsorbent sample of 4 g was used in each experiment, except for squid pen that an 8 g sample was used.

The shaft stirring speed was 400 rpm—the maximum allowed by the equipment, previously showed to be

Table 4
Natural materials' main components and method of analysis of the leached components

Main component	Method of analysis
C	TC/TIC/TOC analyzer
Ca	Atomic absorption spectrophotometry (3500B)[a]
Fe	Atomic absorption spectrophotometry (3500B)[a]
$S–SO_4^{2-}$	Turbidimetry (4500E)[a]
$S–S_2O_3^{2-}$, SO_3^{2-}, S^{2-}	Back titration[b]
Sr	Atomic absorption spectrophotometry (3500B)[a]
Zn	Atomic absorption spectrophotometry (3500B)[a]

[a]Standard methods for the examination of water and wastewater (APHA, AWWA, WEF, 1992).
[b]L'Analise Chimique et Physico-Chimique de L'eau: Eaux Naturelles—Eaux Residuaires (Rodier, 1971).

enough to eliminate the film resistance to mass transfer. A flowrate of 42 cm^3/min was used.

A step perturbation in the inlet dyestuff concentration (CE = 0.054 g/L) was induced and the system response was measured by collecting samples at the adsorber outlet, allowing the determination of the dyestuff concentration and pH histories, at 20 °C.

The air removal from the adsorbent pores, and the measurements of dyestuff concentrations and pH, were conducted as stated in the equilibrium studies.

2.7. Column experiments

Column experiments were performed using a packed jacketed column, working at 20 °C (tap water was used as thermostatic fluid). The dyestuff solution was pumped downflow trough the glass column, with 2 cm inside diameter and 20 cm height, at a 2 cm^3/min flowrate. A smaller column, with 1 cm inside diameter and 10 cm height, was used for the Squid pen experiments.

After weighting the adsorbent, air was removed from the adsorbent pores as previously stated, and the material was then placed inside the column. In the smaller column, 1.27 and 0.53 g samples were used, respectively, for squid pen before and after treatment. In the other column, samples of 3.62 and 22.08 g were used, respectively, for chitin and GAC.

A step perturbation in the inlet dyestuff concentration (CE = 0.054 g/L in all experiments, except for GAC experiments where CE = 0.107 g/L) was induced and the system response was measured by collecting samples at the column outlet, allowing the determination of the dyestuff concentrations and pH histories, as described above.

3. Results and discussion

3.1. Equilibrium batch studies

In previous works it was shown that the materials' adsorption capacities could be very much increased after a very simple and inexpensive chemical treatment, in order to increase their relative chitin content and porosity (Figueiredo et al., 1998b, 2000).

The effect of the chemical treatment was much more noticed in the systems with the reactive dyestuff, the largest molecule, but also in the system Squid pen/direct dyestuff. It seems then interesting to present the results obtained with these four systems.

The experimental equilibrium isotherms for these natural materials, before and after chemical treatment, and their fits to the Langmuir model are shown in Figs. 1–4. The corresponding Langmuir model parameters are presented in Table 5. This simple model seems to represent reasonably the experimental data.

The Anodonta shells and the Sepia pens present higher adsorption capacities for the direct dyestuff than for the reactive dyestuff (Figueiredo, 2002) possibly due to the smaller dimension of the direct dyestuff molecules. The opposite is verified with the Squid pen, which presents the highest adsorption capacity for the reactive dyestuff, probably related with the great affinity between the chitin, around 40% of the material (Knorr, 1984), and the Ni present in the reactive dyestuff (Agboh and Qin, 1997).

The adsorbent with the highest adsorption capacity is the Squid pen, followed by the Sepia pen and Anodonta shell. After the chemical treatment great improvements were achieved, but this relative order was kept, which is probably related to their specific surface areas.

It can be concluded that the changes in the physical and chemical properties of the materials after the chemical treatment (Table 3), mostly the increase in their relative chitin content and porosity (and increase in

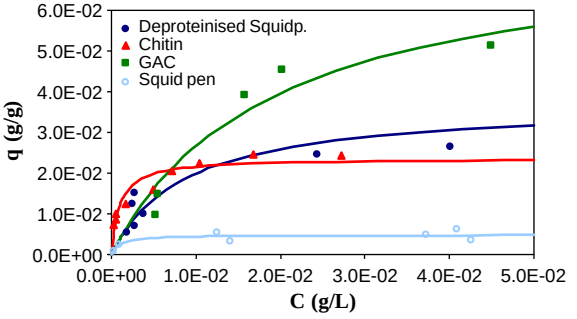


Fig. 1. Equilibrium adsorption isotherms of the CI direct green 26 dyestuff onto Squid pen, before and after deproteinisation, compared with GAC and chitin, and respective Langmuir model fits.

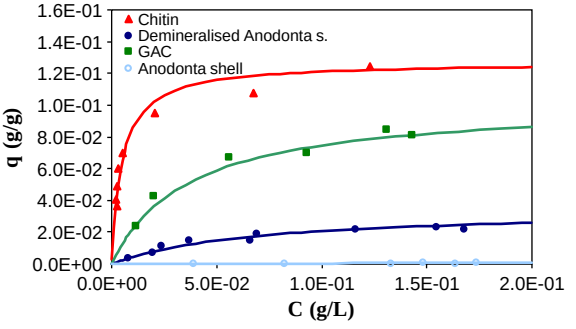


Fig. 2. Equilibrium adsorption isotherms of the CI reactive green 12 dyestuff onto Anodonta shell, before and after demineralisation, compared with GAC and chitin, and respective Langmuir model fits.

specific surface areas and pores sizes), has risen significantly the materials' adsorption capacities. They behave almost like pure chitin and the granular activated carbon studied, as shown in Figs. 1–4. The Langmuir model parameters may be compared between Tables 5 and 6.

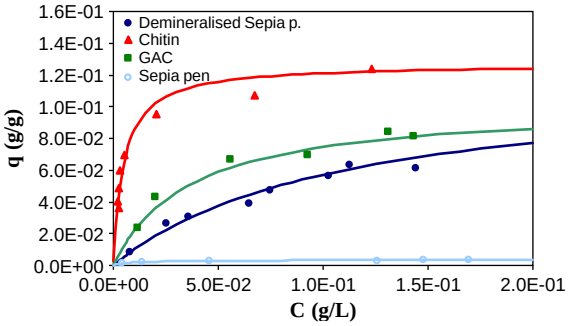


Fig. 3. Equilibrium adsorption isotherms of the CI reactive green 12 dyestuff onto Sepia pen, before and after demineralisation, compared with GAC and chitin, and respective Langmuir model fits.

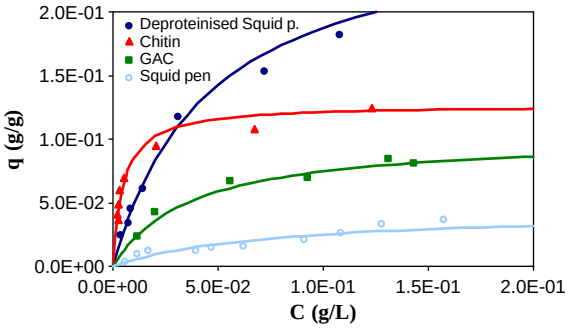


Fig. 4. Equilibrium adsorption isotherms of the CI reactive green 12 dyestuff onto Squid pen, before and after deproteinisation, compared with GAC and chitin, and respective Langmuir model fits.

The deproteinised Squid pens, the best adsorbent used, remove the direct dyestuff as well as or better than pure chitin. They adsorb the reactive dyestuff, in concentrations higher than 0.03 g/L, better than pure chitin and the granular activated carbon studied.

The demineralised Anodonta shells and Sepia pens present adsorption capacities close to the activated carbon studied, but lower than pure chitin.

3.2. Desorption and regeneration experiments

The desorption in distilled water was evaluated for all systems studied. It was observed a slight desorption, of 12%, only for the direct dyestuff adsorbed in the deproteinised Squid pen.

As we are dealing with low-cost adsorbents, the regeneration is not economically attractive, so experiments were only performed for the two systems with higher adsorption capacities, the deproteinised Squid pen with the direct and reactive dyestuffs. Only the deproteinised Squid pen saturated with reactive dyestuff seems to be partially regenerated: 73% regeneration can be achieved using high temperature (79 °C) and 77%, with a 0.1% sodium hydroxide solution is utilised (pH > 12).

3.3. Evaluation of leached components

According to Table 7, the leaching of the most hazardous elements like strontium, iron and zinc is not significant. However there are higher contributions of calcium, sulphur and carbon in the organic (TOC) and inorganic form (TIC). The calcium leached is not environmentally harmful, increasing only the water

Table 5
Langmuir model parameters for the materials before and after chemical treatment, at 20 °C (grain size 0.500–1.41 mm) and respective 95% confidence intervals, variances (σ^2) and correlation coefficients (r)

Adsorbent	Treatment	Langmuir model		σ^2	r
		q_S (g/g)	k_L (cm^3/g)		
Dyestuff: CI direct green 26					
Squid pen	Deproteinisation	3.7E−2±0.9E−2	1.2E+5±1.7E+5	1.8E−5	0.93
	None	4.8E−3±1.4E−3	1.1E+6±2.1E+6	1.1E−6	0.85
Dyestuff: CI reactive green 12					
Anodonta shell	Demineralisation	3.4E−2±0.6E−2	1.5E+4±1.2E+4	4.3E−6	0.97
	None	4.4E−4±1.1E−4	3.8E+4±4.7E+4	9.6E−10	0.86
Sepia pen	Demineralisation	1.2E−1±0.3E−2	9.2E+3±7.3E+3	1.5E−5	0.99
	None	3.5E−3±0.4E−3	1.1E+5±0.7E+5	4.8E−8	0.98
Squid pen	Deproteinisation	2.7E−1±0.4E−1	2.1E+4±0.8E+4	7.2E−5	0.99
	None	4.4E−2±2.7E−2	1.3E+4±1.7E+4	1.9E−5	0.93

Table 6
Langmuir model parameters for the granular activated carbon and chitin (grain size 0.500–1.41 mm), at 20 °C, and respective 95% confidence intervals, variances (σ^2) and correlation coefficients (r)

Adsorbent	Langmuir model		σ^2	r
	q_s (g/g)	k_L (cm^3/g)		
Dyestuff: CI direct green 26				
Chitin	2.4E−2±0.4E−2	1.1E+6±0.8E+6	6.6E−6	0.94
GAC	7.7E−2±3.2E−2	5.3E+4±5.4E+4	2.8E−5	0.97
Dyestuff: CI reactive green 12				
Chitin	1.3E−1±0.1E−1	2.0E+5±0.8E+5	6.6E−5	0.98
GAC	1.0E−1±0.2E−1	2.7E+4±1.9E+4	2.0E−5	0.98

Table 7
Percentual leaching (g of leached component/100 g of adsorbent) for each natural material (grain size < 0.063 mm) after 15 days in distilled water at 20 °C

Adsorbent	TOC	TIC	Ca	Sr	Fe	Zn	S
Anodonta shell	2.7E−2	2.1E−1	2.5E−1	4.0E−4	<2.3E−4	< 3.7E−5	1.8E−2
Sepia pen	1.4E−1	3.9E−1	5.1E−1	7.2E−3	<2.5E−4	1.7E−4	1.2E−2
Squid pen	3.1	2.7	1.8E−1	< 5.0E−4	< 6.2E−4	< 1.0E−4	3.0E−1

hardness (usually low in the rivers in the North of Portugal). Associated with calcium is the presence of carbonate ions (measured by TIC), mostly in the Anodonta shell and Sepia pen that are composed by crystalline calcium carbonate. They contribute to an increase of the water alkalinity and pH at the column outlet. Although the leaching of organic matter (measured by TOC) and sulphur are undesirable, a good control of the operating conditions regarding oxygenation, apart from increasing the dyestuff's biodegradation, avoids the anaerobic degradation of organic matter and the reduction of sulphur compounds to sulphides during the adsorption process.

3.4. Continuous stirred tank adsorber studies

Previous studies (Figueiredo, 2002) were performed to find operating conditions that minimise the external mass transfer resistance. When a 67.5 cm^3/min flowrate and 243 rpm stirring speed were used, the system's (without adsorbent) response to a tracer injection (2 mL of potassium chloride 3 M) was the same as that obtained in a perfectly mixed continuously stirred adsorber. For different flowrates of the direct dyestuff solution (42 and 67.5 cm^3/min) and stirring speeds (243, 400 and 589 rpm), the system's answer to a step perturbation was the same. This seems to prove that in these operating conditions the fluid was perfectly mixed, however, the adsorbent baskets themselves might have introduced a resistance to mass transfer.

It has been proved, by the mathematical simulation of the experiments, that the maximum stirring rate used in this work, 400 rpm at a 42 cm^3/min flowrate, was enough to eliminate the external mass transfer resistance, allowing the determination of the internal resistance. The mathematical simulation of the experiments was performed using a pore diffusion model (Figueiredo et al., 2001) that used the equilibrium data determined and had as the only unknown parameter the internal mass transfer resistance.

The mathematical simulation of the experiments performed for all the natural adsorbents, before and after chemical treatment, suggests the existence of a high internal resistance in all the systems, which can be related with the low molecular diffusivity of the reactive and direct dyestuffs used in this work, respectively, 1.19E−6 and 1.44E−6 cm^2/s, estimated using the Wilke and Chang correlation (Reid et al., 1987). This was somehow expected due to the high molecular weight of the reactive and direct dyestuffs, respectively, 1837.4 and 1338.1.

For example, Fig. 5 presents the experiments with Squid pen before and after chemical treatment, using the direct dyestuff, and their mathematical simulations. They were obtained using the equilibrium parameters previously determined and tortuosity values estimated by the Neale and Nader correlation (Loureiro, 1986), 1.44 and 1.35, respectively, and correspond to a number of internal mass transfer units (N_d) of 0.185 and 0.360 (respectively, $\xi N_d = 0.125$ and 0.714). These very low

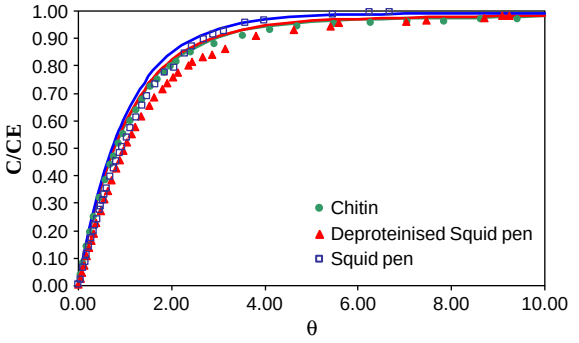


Fig. 5. Experimental runs in the Carberry-type adsorber using the CI direct green 26 dyestuff with Squid pen, before and after deproteinisation, compared with chitin, and respective simulated curves.

values, indicating high internal resistance, are due to the low internal diffusivity of the direct dyestuff, in spite of the low tortuosity values used, near the lowest value with physical meaning, 1.

In the same Fig. 5 it is shown the experiment for the same dyestuff adsorbed on chitin and the simulated curve obtained using the equilibrium data already determined and a 1.31 tortuosity value, also estimated by the Neale and Nader correlation (Loureiro, 1986). This corresponds to a number of internal mass transfer units (N_d) of 0.388 ($\xi N_d = 0.69$), indicating again a high internal resistance.

If the curves presented in Fig. 5 were simulated with tortuosity 1 they would be plotted practically in the same position as the ones represented. The low molecular diffusivity of the dyestuff is responsible for the low N_d values, in such way that the tortuosity (the only adjustable parameter of these mathematical simulations, always $\geqslant 1$) cannot compensate the low value of the estimated molecular diffusivity and so result in lower estimated values for the internal resistance.

3.5. Column experiments

The fixed bed column experiments performed with the natural adsorbents before and after chemical treatment show an improvement in their behaviour, as verified in the batch equilibrium studies.

It is interesting to notice that in the two systems where the chemical treatment did not produce great improvements in the adsorption of the direct dyestuff, i.e., when Anodonta shell or Sepia pen were used, a biodegradation reaction of the dyestuff occurred. This was also verified in some batch tests, the ones with the higher amounts of dyestuff, and it is possible that the microorganisms present (a mixed culture of yeasts and bacteria) were introduced with the adsorbent (Figueiredo, 2002). It should be remarked that the extreme pH conditions used in the chemical treatments would probably prevent the microrganisms' survival.

This biodegradation was definitively proved in the column experiments where the outlet dyestuff concentration increased only during an initial period and after that converged to a steady-state value. In order to determine the biodegradation reaction kinetic constant (supposed to be of first order) flowrate variations were induced. These provoked variations in the column mean residence time which led to Damköhler number proportional changes. If the column is considered to operate as a plug flow reactor, its conversion ($=1-C/CE$) at the end of the column depends only of the Damköhler number. This allowed values of 1.25E−3 and 1.40E−3 s^{-1} to be obtained for the apparent first order biodegradation kinetic constant, respectively, for the Anodonta shell and Sepia pen/direct dyestuff systems.

The biomass sample collected from the inside of the column outlet tube showed also significant oxygen and dyestuff uptakes, 0.16 and 0.51 mg/(mg TSS.d), respectively (Figueiredo et al., 1998a, 2000). The occurrence of this biodegradation reaction was the main mechanism of dyestuff removal and adsorption was strongly reduced by the pore clogging effect of the biomass. The biological degradation of the dyestuff has the advantage of preventing adsorbent saturation and makes regeneration unnecessary. This is called bioregeneration by some authors (Chudyk and Snoeyink, 1984).

The equilibrium and kinetic data, independently obtained, were used in a "complete" model (including pore diffusion, film mass transfer, axial dispersion and a first order biodegradation reaction) to simulate the fixed bed experiments performed (Figueiredo et al., 2000). These mathematical simulations allow us the determination of the external mass transfer coefficient (k_f), as the only unknown parameter—initially estimated by the Wilson and Geankoplis correlation (Ruthven, 1984). At the same time it is possible to compare the adsorbents' performances, namely before and after treatment, based on the simulation parameters used.

For example, Fig. 6 presents the column experiments using the direct dyestuff with Squid pen before and after treatment and their mathematical simulation. The simulated curves do not follow completely the experimental data, maybe due to the linear driving force model approach (not advisable for systems with high internal resistances) or to the heterogeneous nature of the materials used (responsible for variability in the materials' properties). On the other hand there was a range of k_f values possible for the same experiment, showing a low system sensitivity to the k_f variation, because the high internal resistance was the dominating resistance.

Albeit the existence of these limitations it is possible to compare the simulation parameters for the system Squid

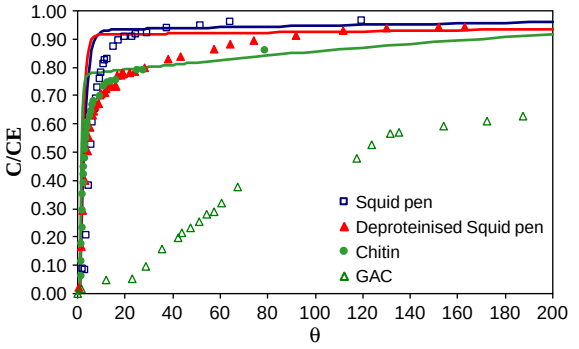


Fig. 6. Experimental runs in the fixed bed column using the CI direct green 26 dyestuff with Squid pen, before and after deproteinisation, compared with chitin and GAC, and respective simulated curves.

pen/direct dyestuff ($Pe = 80$, $N_f = 0.27$, $\xi = 25$, $N_d = 1.1E{-}6$, $\xi N_d = 2.7E{-}5$) with the ones for the system deproteinised Squid pen/direct dyestuff ($Pe = 128$, $N_f = 0.13$, $\xi = 50$, $N_d = 4.8E{-}5$, $\xi N_d = 2.4E{-}3$). After the chemical treatment the column capacity factor has doubled and the internal resistance, evaluated through ξN_d, has decreased approximately 100-fold.

The column experiments performed in the same operation conditions with pure chitin and granular activated carbon are compared with the run using deproteinised Squid pen in the same Fig. 6.

The best mathematical simulation of the chitin run was made using a tortuosity value, 42, higher than the ones used in the stirred tank experiments. It is possible to compare the dimensionless parameters of this run ($Pe = 184$, $N_f = 0.63$, $\xi = 42$, $N_d = 2.0E{-}6$, $\xi N_d = 8.4E{-}5$) with the ones of the deproteinised material, with the already stated limitations. They present similar column capacity factors, but the internal resistance evaluated trough the ξN_d value is even lower for the deproteinised Squid pen (this may be related to the high tortuosity value used in the chitin run mathematical simulation).

The deproteinised Squid pen performs almost like pure chitin, but not as well as the granular activated carbon tested.

The same behaviour was observed for the reactive dyestuff, when the column experiments performed with the Anodonta shell, Sepia pen and Squid pen, before and after chemical treatment, are compared with pure chitin and granular activated carbon.

The high specific surface area of the studied granular activated carbon (900–1000 m^2/g) and its porous structure, with macropores and mesopores, allow an easier penetration of the large dyestuff molecules (in this case micropores are inaccessible to them), which can be related with much lower internal resistances to mass transfer than those observed in the natural materials before and after chemical treatment.

As adsorption in the granular activated carbon micropores is prevented for the large adsorbate molecules, the adsorption capacities already shown in Table 6 are low (when compared with typical adsorption capacities with the same specific surface area), but in this particular case the most important factor is the rapid accessibility of the adsorbate to the adsorption sites.

4. Conclusions

The natural materials—Anodonta shell, Sepia and Squid pens—after chemical treatment increased their relative chitin content. This may explain the increase in the adsorption capacities for the reactive dyestuff, knowing the great chemical affinity nickel/chitin, together with the improvement in their physical characteristics as adsorbents, mostly due to an increase in specific surface area, porosity and average pore size diameter.

The increase in the adsorption capacity of the direct dyestuff was only verified with the deproteinised Squid pen. This was the natural material with higher specific surface area (8.82 m^2/g) but with the lowest average pore size diameter (45.7 nm, compared to more than 70 nm in the Anodonta shell and Squid pen). The low pore size diameter prevented the adsorption of the direct dyestuff, but after the chemical treatment this size almost doubled, allowing the molecules' migration to the adsorption sites, and with a larger specific surface area (12.2 m^2/g).

The equilibrium data and the parameters used for the mathematical simulation of the Carberry-type continuous adsorber and fixed bed experiments led us to the conclusion that the systems natural adsorbent/textile dyestuff studied present very high internal resistances, even after the chemical treatment. This is related to the high molecular weight of the direct and reactive dyestuffs studied, responsible for the very low molecular diffusivities estimated.

It was observed that in fixed bed column experiments, 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.

Combining biodegradation and adsorption in the column experiments, the adsorbents showed similar or better performances than the chitin itself, but not as good as the activated carbon studied. Besides presenting similar adsorption capacities, the carbon porous structure is much more accessible to the dyestuff molecules, which is of great importance to the dyestuffs' uptake kinetics.

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