Use of non-treated shrimp-shells for textile dye removal from wastewater

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ABSTRACT

This paper investigates the removal of direct dyes through adsorption on chitin-containing residues. As representative waste, the shells of two shrimp species are tested. Removal percentage up to 90% for the tested dyes are obtained in about 2 h, using 2.1 mg mL^{-1} of shells, simply dried and grinded. Comparative analyses are also conducted on commercial chitin and chitosan flakes. Kinetic tests are carried out in batch and at lab scale. Data are modeled through the pseudo second-order kinetic law, and a value of modeling efficiency close to 1 is obtained. Adsorption isotherms are traced with the temperature varying between 10 °C and 50 °C. The results are first analyzed using the Langmuir expression, and then interpreted following a statistical physics approach to obtain a deeper understanding of the phenomenon at the molecular level. The anchorage number, the steric hindrance coefficient, and the half saturation coefficient are derived. All experimental data indicate a monolayer adsorption process that is limited to the existing micro-porosity, favored by concentration gradient diffusion, and characterized by several anchorage points for each single molecule.

1. Introduction

According to the available data [1], about 14 thousand tons of textile dyes are discharged into the environment each year, causing severe consequences to the environmental quality [2–5]. Although the most efficient system for textile dye removal is probably adsorption [2,4,6–8], the cost of traditional adsorbents is very high and often discourages their use [9,10]. To improve the economics of environmental sustainability, new materials have been tested for dye adsorption [6,11]. Among these materials, chitin/chitosan-derived compounds seem to be particularly appealing [12–15]. Chitin is the most abundant natural polysaccharide after cellulose and can be obtained from many different sources at a low cost, and chitosan can be easily produced by the de-acetylation of chitin [16]. Tested chitin/chitosan-derived materials include chitosan resins, cross-linked biopolymers, chitin/chitosan immobilized beads, gel, fibers, and many others [2,10,17]. Unfortunately, the use of chitin/chitosan derivatives does not ensure a given removal efficiency, as the efficiency is extremely dependent on the derivation process and on the material's origin and characteristics, such as its crystallinity, solubility, and degree of N-acetylation

[2,4,18]. Recently, some researchers have focused on the use of chitin/chitosan-containing residues (mainly from seafood shells) without any modification [15–19]. This keeps the cost of the adsorbent production close to zero, and no waste results from the derivation process [4,6,20,21].

Starting from this premise, the present paper investigates the removal of direct dyes using raw chitin-containing residues, analyzes some aspects that have been missed [6], and compares the obtained performance with that using pure chitin and chitosan flakes. The decision to study direct dyes was made since they have been less investigated than other dyes, despite their frequent release into wastewater, for example, during the washing of colored fabrics.

The aim of this study is better understand the mechanisms involved in the adsorption process in order to promote full-scale application of the system. Together with traditional investigations concerning process kinetics and adsorption isotherms, this study includes a physicochemical interpretation of the data at the molecular level based on a statistical physics theory approach [7,22–26]; this allows a better understanding of the tested processes.

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2. Material and methods

The study was conducted using shrimp shells obtained from the fish market in Naples (Italy). Before use, the shells were rinsed several times with tap water, sun-dried for 24 h, and finely ground using a common laboratory blender. The shells of two edible species, namely *Aristaeomorpha foliacea* (*A.f.*) and *Aristeus antennatus* (*A.a.*), were tested to investigate any differences in adsorption capacity. Comparative tests were conducted using chitin and chitosan flakes (Sigma Aldrich, Italy) that originated from shells.

Fig. 1 reports the SEM image obtained on *Aristaeomorpha foliacea* shells after grinding, using a scanning electron microscope (Zeiss, Germany) equipped with a digital energy dispersive X-ray detector (Oxford Instruments, England), while Table 1 summarizes the results obtained through BET surface analysis performed using a Chimeisorb-2750 (Micrometrics, USA). The observable scaly structure of the shells resulted quite regular and presented no notable features, in agreement with data reported in previous studies [20,21]. The specific surface area (S_A) and the total pore volume (P_V) resulted much smaller compared to the values of traditional adsorbents [27,28], although not substantially different from those obtained for chitosan flakes prepared from fishery residues [10].

The research was performed on synthetic wastewater containing a mixture of two direct dyes purchased from Sigma Aldrich (Italy): Direct Red 80 (DR80) and Direct Blue 71 (DB71). Both dyes are in the class of the poly-azo-dyes, and are derivatives of the so-called I-Acid (7-amino-4-Hydroxy naphthalene-2-sulphonic acid). DR80 is a derivative of the dimeric I-Acid. The I-Acid dimer is coupled in position 3 and 3 to two azo building blocks as follows: [aniline – 4 – sulphonic acid aniline – 2 – sulphonic acid I acid] 2 – C=O. Similarly DB71 has the following building blocks: 3-amino naphthalene – 1,5 – disulphonic acid 1-amino naphthalene 8 – amino naphthalene – 2 – sulphonic acid I Acid. The synthetic wastewater was prepared by adding $0.8\,g\,L^{-1}$ of DR80 and $10\,g\,L^{-1}$ of DB71 to de-ionized (DI) water containing sodium chloride ($5\,g\,L^{-1}$) and sodium carbonate ($2\,g\,L^{-1}$). The obtained stock solution was stabilized through three cycles of heating ($60\,°C$ for 1 h) and cooling ($22\,°C$ for 24 h). Before use the solution was diluted with DI water at 1:100 v/v. The composition was chosen to simulate a real wastewater produced in a small textile industry close to Naples (South of Italy), which was used for a final confirmative test. To compare results obtained for varying water characteristics, different dilution values were also tested ranging from 1:25 to 1:200, while pH was varied between 5.5 and 8.5. All experiments

Table 1
Results of BET surface analysis performed on the used shrimp shells.

	S_A ($m^2\,g^{-1}$)	P_V ($m^3\,g^{-1}$)
Aristeus antennatus	16.54	0.0051
Aristeomorpha foliacea	17.37	0.0055

were conducted on replicates at lab scale in 50 mL volume glass reactors that were continuously mixed using an orbital shaker (Analytical Control De Mori, Italy). The reaction time varied between 15 min and 24 h and the adsorbent was removed from the treated wastewater by filtration using a $0.8\,\mu m$ paper filter. Blank tests were performed to exclude the effect of dye removal due to phenomena other than adsorption. Dye removal was evaluated using a Photo Lab 6600 UV–vis spectrophotometer (WTW GmbH, Germany) to measure the residual absorbance at 527 nm for DR80 and 592 nm for DB71, corresponding to the absorbance peaks of the dyes. Before use, all glasses were soaked overnight in a nitric acid bath and rinsed several times with DI water. The used reagents were of analytical grade, except the chitin and chitosan flakes, which were of practical grade.

3. Results and discussion

3.1. Kinetic tests

The results of the kinetic tests are summarized in Figs. 2–4 . Figures refer to tests conducted at pH 6.5. As can be easily seen, the removal efficiency increased with time until it reached an asymptotic value after about 10–12 h (Fig. 2). The trend was the same for the two tested dyes, and no significant differences were obtained using the shells of *Aristaeomorpha foliacea* instead of the shells of *Aristeus antennatus*. The removal rate was higher during the first 5 h and then started decreasing until it plateaued. This trend was attributed to the successive saturation of sites directly available for adsorption [2,15,17] and to the instauration of a dynamic equilibrium between adsorbed and released molecules [6]. In agreement with this description of the adsorption phenomenon, increasing the amount of the adsorbent resulted in a linear increase in the removal rate for the first 3 h of the reaction (Fig. 3). However, at longer reaction times, a linear increase in the removal rate was observed only for shell doses up to $2.5\,mg\,mL^{-1}$, while for higher doses, the removal rate remained constant or even decreased. This was a consequence of the mutual interaction of available sites, which tend to overlap or aggregate [15]. Data obtained varying pH showed no notable differences (data not shown): removal efficiency remained in the same range, with maximum variability included in the range of triplicates
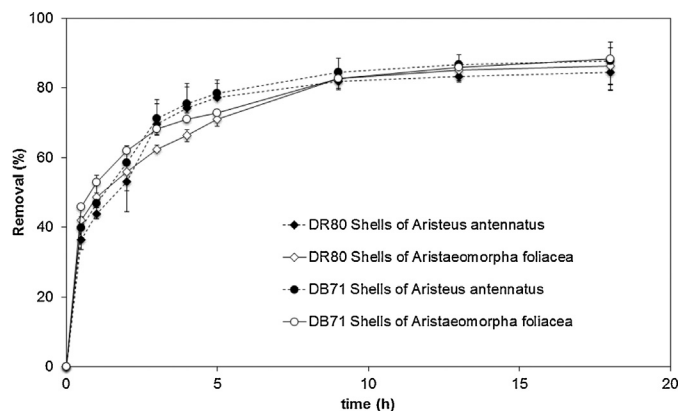

Fig. 1. SEM image of used shells.

Fig. 2. Dye removal percentage at 25 °C and pH 6.5 using $2.1\,mg\,mL^{-1}$ adsorbent.