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Spent Tea Leaves as a Potential Low-cost Adsorbent for the Removal of Azo Dyes from Wastewater

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Spent tea leaves (STL), a solid waste that is available in large amounts worldwide, was investigated as a potential low-cost adsorbent for the removal of two azo dyes, Reactive Green 19 (RG19) and Reactive Violet 5 (RV5), from contaminated waters. Preliminary experiments conducted on untreated STL showed that this material exhibited very low removal efficiencies (<10 %). By contrast, thermal activation of STL (200 to 400 °C for up to 2 h) resulted in a significant increase in dye adsorption. After thermal exposure of STL to 300 °C for 1 hour, removal efficiencies of 98.8 % and 72.8 % were observed, respectively, for RG19 and RV5. Characterization of the adsorbent by TG/DTA and FTIR measurements showed that structural and chemical changes occurred in the lignocellulosic material which were probably responsible for the enhancement in adsorption capacity. These results strongly support the use of activated STL as a low-cost alternative to conventional adsorbents.

1. Introduction

The use of azo dyes for textile dyeing has increased considerably over the last years because of their cost effectiveness and the variety of colours available (Chang et al., 2004). When applied to fabrics, reactive groups in the dye molecule form stable covalent bonds with the fibers, imparting a bright and lasting color to the final product. However, their low degree of fixation on the fiber, typically between 50 and 90 %, results in the release of substantial amounts of the dye in the wastewater (Jonstrup et al., 2011). It is estimated that about 280,000 t of dyes are discharged annually in effluents from textile dyeing industries (Jin et al., 2007). If improperly treated, these effluents may have a significant impact on the environment. In particular, they may cause a reduction in sunlight penetration and dissolved oxygen concentration in the receiving water bodies and deleterious effects on local flora and fauna. For these reasons, contamination by azo dyes is considered a major environmental problem.
Several abatement technologies, including adsorption (Mohammed et al., 2011), microbial degradation (Casaletto et al., 2011) and advanced oxidation processes (Zuorro et al., 2013), have been proposed for removal of azo dyes from textile effluents. Adsorption is one of the most effective methods and activated carbon is the most commonly used adsorbent. However, despite its inherent advantages, such as efficiency and versatility, carbon adsorption remains an expensive process. This fact has prompted a growing interest into the production of low-cost alternatives to activated carbons (Gupta and Suhas, 2009). A low-cost adsorbent is defined as one which is abundant in nature, or is a by-product or waste from industry and requires little or no processing.
In this contribution we have investigated the suitability of spent tea leaves (STL) to remove azo dyes from aqueous solution. After water, tea is the most widely consumed beverage in the world, as attested by the over 3,000,000 tons of tea leaves produced each year (Wan and Zhang, 2008). Although available in different varieties, such as green, black or Oolong tea, all tea beverages are obtained from the same basic tea (*Camellia sinensis* L.) leaves. Once the beverage has been brewed, STL become a waste that must be disposed of. Thus, like other biomass residues, STL represent one of the many waste materials destined for landfill as well as an unused resource (Arvanitoyannis and Varzakas, 2008).
Studies over the last decade have demonstrated that STL can be effectively used for the removal of different types of pollutants from water, including arsenic (Murugesan et al., 2006), methylene blue

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(Hameed, 2009) and heavy metal ions such as zinc (Wasewar et al., 2009) and lead (Lavecchia et al., 2010). However, no report has so far been published on the use of STL to remove azo dyes from aqueous solutions. In this study, we examined the adsorption of two commercial azo dyes, Reactive Green 19 (RG19) and Reactive Violet 5 (RV5), on STL, with the aim to provide further information on the potential of this waste as a low-cost alternative to conventional adsorbents.

2. Experimental

2.1 Materials

RG19 and RV5 were obtained in solid form from Gammacolor Srl (Seveso, Italy) and used as received. Some characteristics of the dyes are given in Table 1. Dye solutions were prepared by dissolving appropriate amounts of the compounds in distilled water.

Methylene blue, activated carbon and Fuller's earth were from Sigma-Aldrich (Milano, Italy). All other chemicals were of analytical grade and used without further purification.

2.2 Preparation of adsorbent

Black tea from commercial tea bags was used to obtain STL. Tea infusions were first prepared by steeping some tea bags in tap water (125 mL of water per tea bag) at 90 °C for 3 min. After this time, STL were recovered and repeatedly washed with distilled water in order to remove soluble and colored compounds. The solid was then rinsed and oven dried at 60 °C for 24 h. Finally, STL were ground, sieved to <500 μm and stored in polyethylene bags at room temperature until use.

Thermal activation of STL was carried out in a muffle furnace by stepwise increase of the temperature (up to 400 °C) and isothermal heating for a time of 0.5 to 2 h.

2.3 Analytical methods

Dye concentrations were determined spectrophotometrically using a double-beam Lambda 25 spectrophotometer (Perkin Elmer, USA). Measurements were made at the respective λ_{max} values (630 nm for RG19 and 560 nm for RV5) against a blank of distilled water. Absorbance values were converted to concentrations by using calibration curves obtained from dye standards (Zuorro and Lavecchia, 2013).

Moisture content was measured by a MAC 50/1 electronic moisture analyzer (Radwag, Poland) and the particle size distribution was determined by dynamic light scattering with a Malvern Particle Sizer (Malvern Instruments, UK).

FTIR spectra were acquired in the mid-IR region (4000–400 cm^{-1}) using a Bruker Vertex 70 spectrometer equipped with a Platinum ATR sampling module.

TG-DTA measurements were carried out between 30 and 900 °C with an SDT Q600 analyzer (TA Instruments, USA).

2.4 Adsorption studies

Adsorption experiments were performed in batch mode in 50 mL screw-top flasks. Appropriate amounts of STL and the dye solution were initially loaded into the flasks thermostated at 25 ± 0.1 °C and magnetically stirred for the required time. Then, the flask content was centrifuged at 10,000 × g for 10 min. The supernatant was filtered at 45 μm and analyzed for dye concentration. The initial dye concentration was varied between 50 and 100 mg L^{-1} and the liquid-to-solid ratio between 50 and 150 mL g^{-1}.

The amount of adsorbed dye (Q) and the dye removal efficiency (E) were calculated according to the following expressions:

$$Q = \frac{(c_0 - c_t)V}{m_S}, \qquad E = \frac{c_0 - c_t}{c_0} \times 100 \tag{1}$$

where c_0 and c_t represent the initial and final dye concentrations, V is the volume of the solution and m_s is the mass of adsorbent.

Table 1: Some characteristics of the azo dyes RG19 and RV5

	RG19	RV5
Chemical class	Anionic, diazo	Anionic, monoazo
CAS number	61931-49-5	12226-38-9
Color index number	68110-31-6	18097
Molecular formula	$C_{40}H_{23}Cl_2N_{15}Na_6O_{19}S_6$	$C_{20}H_{16}N_3Na_3O_{15}S_4$
Molecular weight (g mol^{-1})	1418.93	735.58
λ_{max} (nm)	630	560

3. Results and discussion

A first series of experiments was designed to assess the adsorption properties of untreated STL for the azo dyes. Then, STL were subjected to a thermal treatment under different time-temperature conditions and the effects on dye adsorption were assayed. Finally, the adsorption capacity of thermally treated STL was compared with those of two conventional adsorbents: activated carbon and Fuller's earth.

3.1 Dye adsorption on untreated STL

These experiments were performed at 25 °C on dye solutions at 50 mg L^{-1} using a contact time of 1 h and varying the solid-to-liquid ratio from approximately 5 to 40 g L^{-1}. Some representative results are reported in Table 2. It can be seen that the observed removal efficiencies were very low (<7 % for RG19 and <6 % for RV5). In addition, only minor variations in the adsorption efficiency were observed by increasing the adsorbent dose, indicating the poor affinity of STL for the two azo dyes.

A possible explanation for the above behaviour can be found in the unfavourable electrostatic interactions between the dye molecules and the adsorbent surface. It is known, in fact, that lignocellulosic plant materials like STL contain negatively charged surface sites, including the hydroxyl and carboxyl groups on **the cellulose fibers (**Zuorro et al., 2011) or those present in proteins and phenolic compounds (Demirbas, 2008). These groups are considered the main responsible for the binding of negatively charged heavy metal ions by STL (Zuorro and Lavecchia, 2010). To lend support to this hypothesis, we carried out some experiments with methylene blue as adsorbate. Methylene blue is a cationic dye, which exists in aqueous solution in the form of positively charged ions. The experiments were conducted under the following conditions: T = 25 °C, c_0 = 50 mg L^{-1}, S/L = 6.6 g L^{-1}, t = 1 h. The measured removal efficiency was 97.85 %, against the values of 1.61 % and 1.03 % determined, respectively, for RG19 and or RV5 (see Table 2). Accordingly, it can be concluded that the limited adsorption of the azo dyes examined on STL is mainly due to the repulsive electrostatic interactions with the adsorbent surface.

3.2 Dye adsorption on thermally-treated STL

To improve the adsorption performance of STL, they were subjected to a thermal activation process consisting of: (1) heating the waste material to a temperature of 200, 300 or 400 °C; (2) exposure to that temperature for 1 to 2 h and (3) cooling down to room temperature. Thermally treated STL were then assayed for their adsorption efficiency. Some representative results, relative to an exposure time of 1 h at the treatment temperature, are shown in Figure 1. As is evident, a significant enhancement in dye adsorption was achieved, the observed removal efficiencies reaching a value close to 100 % under the most favourable conditions. We also found that the high-temperature treatment caused a considerable mass reduction of the solid material, the measured weight loss being between 53.3 % and 90.2 % (Table 3). Examination of these data together with the resulting dye removal efficiencies suggests that heating STL at 300 °C for 1 h could be a good compromise between the adsorbent loss and the enhancement of adsorption capacity.

Table 2: Amount of adsorbed dye (Q) and removal efficiency (E) for RG19 and RV5 (T = 25 °C, c_0 = 50 mg L^{-1}, t = 1 h). S/L is the solid-to-liquid ratio

Azo dye	*S/L* (g L^{-1})	*Q* (mg g^{-1})	*E* (%)
RG19	6.6	0.129 ± 0.011	1.61 ± 0.14
	13.3	0.150 ± 0.010	3.70 ± 0.24
	20.0	0.181 ± 0.021	6.75 ± 0.78
RV5	6.6	0.079 ± 0.026	1.03 ± 0.33
	13.3	0.110 ± 0.013	2.91 ± 0.33
	20.0	0.133 ± 0.028	5.18 ± 1.11

Table 3: Weight loss (Δw) of STL subjected to the thermal treatment. t_{exp} is the time of exposure at the temperature T

T (°C)	t_{exp} (h)	*Δw* (%)	*T* (°C)	t_{exp} (h)	*Δw* (%)
300	1.0	74.2 ± 0.6	200	1.0	53.3 ± 0.5
300	1.5	76.7 ± 0.4	400	1.0	90.2 ± 0.9
300	2.0	81.0 ± 1.1			

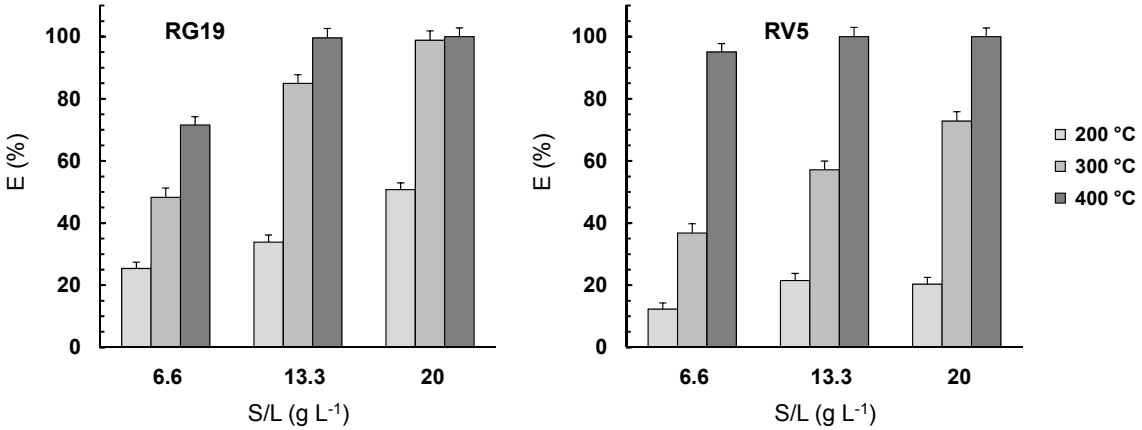
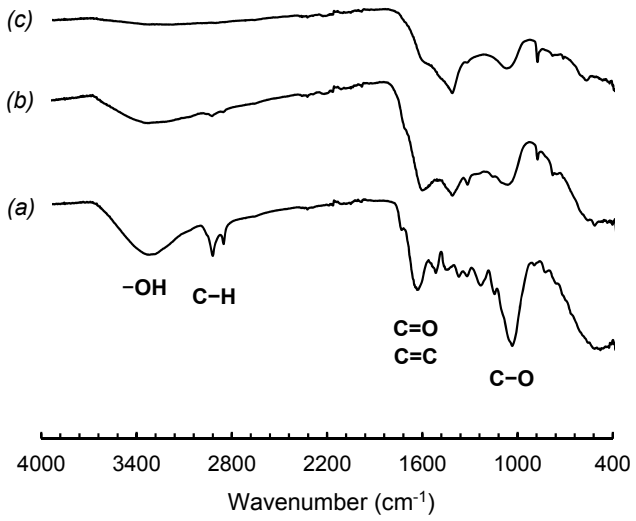


Figure 1: Removal efficiencies of RG19 and RV5 by STL subjected to 1-h heating at 200, 300 or 400 °C (adsorption conditions: T = 25 °C, c_0 = 50 mg L^{-1}, t = 1 h)

FTIR spectra of untreated and thermally treated STL are shown in Figure 2. As can be seen, the spectrum of untreated STL (Figure 2 *a*) displays a number of peaks arising from the absorption of different functional groups in this material. The broad band at about 3400 cm^{-1} can be attributed to bonded –OH groups. The peaks at 2950–2900 cm^{-1} correspond to aliphatic C–H groups. The peak at about 1650 cm^{-1} can be due to C=O or C=C groups, while the peak at about 1100 cm^{-1} can be attributed to C–O stretching of ether groups.

A severe reduction in the intensity of these peaks was observed after subjecting STL to the thermal treatment (Figure 2 *b* and *c*). These changes suggest that major structural and/or chemical modifications occur upon heating. They are probably due to more or less extensive degradation of the cellulose and hemicellulose components of tea leaves. These processes start at about 250–300 °C and occur by the cleavage of C–H, C–O and C–C bonds as well as by dehydration, decarboxylation and decarbonisation (Miller and Bellan, 1997). By contrast, lignin degradation proceeds at higher temperatures, typically around 400 °C, and results in the formation of a variety of products, most of which having phenolic –OH groups (Brebu and Vasile, 2010). These structural transformations are also evident from TG-DTA curves (Figure 3). In particular, the derivative weight curve displays three main endothermic peaks, at about 65, 300 and 450 °C, which can be attributed, respectively, to the loss of hygroscopic water and to cellulose and lignin degradation.



F*igure 2: FTIR spectra of: (a) untreated STL; (b) STL subjected to 1-h heating at 200 °C and (c) STL subjected to 1-h heating at 300 °C)*

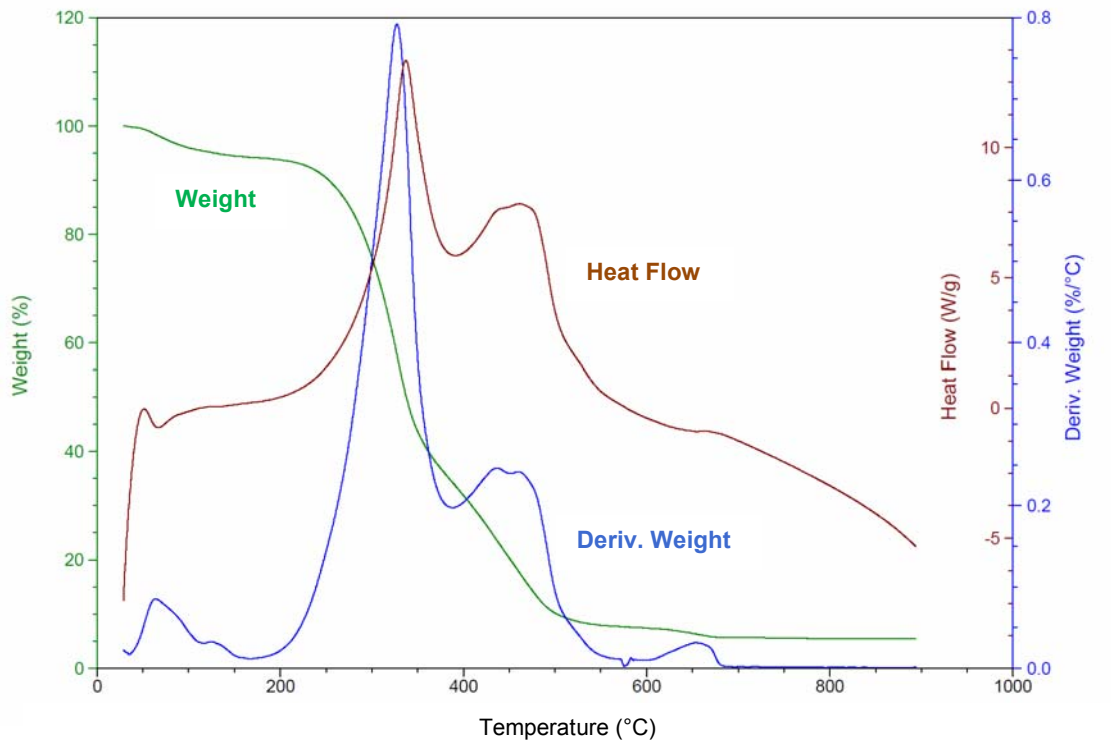


Figure 3: TG-DTA curves of STL

As a result of the above-described transformations, new adsorption sites with higher affinity for the two azo dyes are likely to be created. Of course, the same transformations could also produce an increase in surface area which could contribute to the observed enhancement in dye adsorption.

3.3 Comparison with other adsorbents

Comparison experiments were performed with the following adsorbents: untreated STL, thermally treated (1 hour at 300 °C) STL, activated carbon and Fuller's earth. Each material was contacted at 25 °C with a dye solution at 50 mg L^{-1} for 1 h using a solid-to-liquid ratio (S/L) ranging from 6.6 to 20 g L^{-1}. The results displayed in Figure 4 indicate that the removal efficiencies of RG19 and RV5 by thermally treated STL were comparable or even better than those observed using activated carbon as adsorbent. Fuller's earth was not a good adsorbent for the two dyes, its efficiency being comparable to that of untreated STL. Therefore, in terms of material performance and environmental sustainability, STL can be regarded as very promising candidates for implementation in wastewater treatment of textile dyeing and finishing industries.

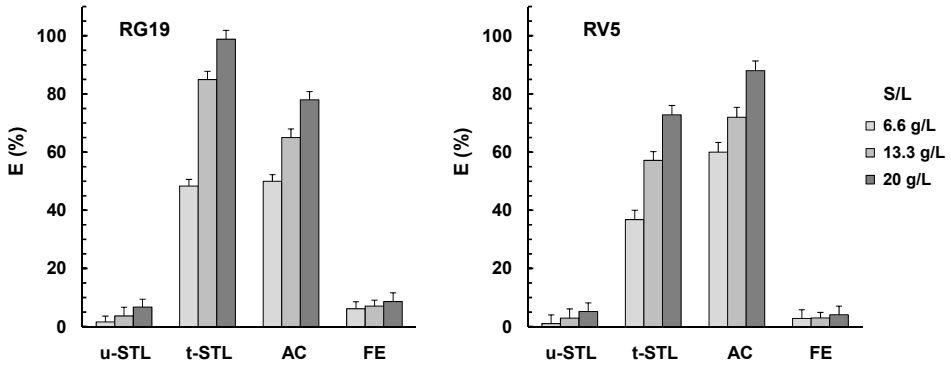


Figure 4: Removal efficiencies of RG19 and RV5 by untreated STL (u-STL), STL subjected to 1-h heating at 300 °C (t-STL), activated carbon (AC) and Fuller's earth (FE)

4. Conclusions

In recent years, several strategies have been proposed for the utilization of vegetable wastes, including the recovery of energy (Marone et al., 2012) or value-added products (Lavecchia and Zuorro, 2008) or the use as adsorbent materials (Patel, 2012).

STL are produced in huge amounts in nearly all parts of the world and their disposal is not devoid of environmental side effects. The results of this study suggest that they could be effectively used as an innovative adsorbent for the removal of azo dyes from textile wastewater. Of course, further research is needed to elucidate the underlying mechanisms and determine the optimum process conditions, together with a cost-benefit analysis to assess the implementation of these new adsorbents on a large scale.

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