

Supporting materials

An alternative use of olive pomace as a wide-ranging bioremediation strategy to adsorb and recover dangerous disperse orange and red industrial dyes from wastewater

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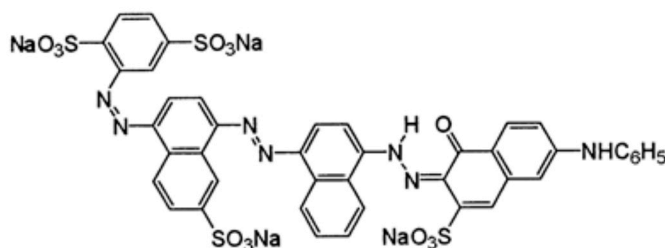
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dB



Scheme S1: Chemical structure of Direct Blue 73 (dB).

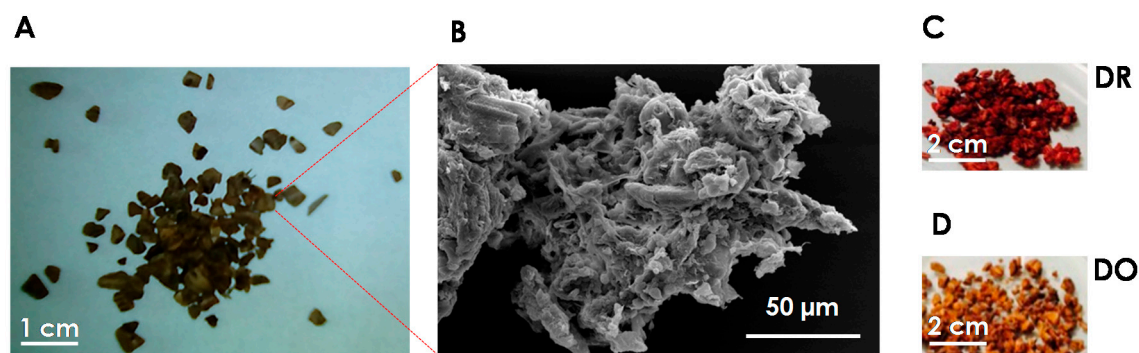


Figure S1: Camera pictures of Olive Pomace, OP (A, scale bar 1 cm), with the related SEM image (scale bar 50 μm) (B); OP as appears after the adsorption of Disperse Red, DR (C) and Disperse Orange DO (D) dye molecules from water, (scale bar 2 cm).

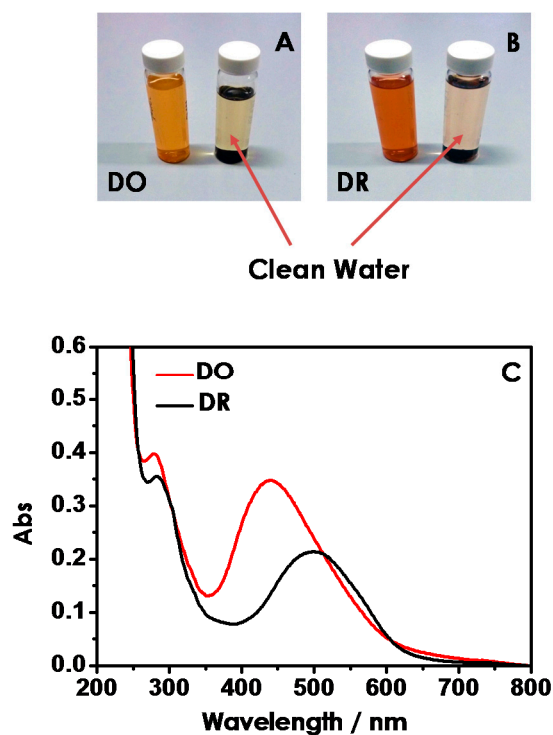


Figure S2: Camera pictures of Disperse Orange, DO (A) and Disperse Red, DR (B) solutions in presence of olive pomace, before and after the adsorption process. Solutions were referred to aqueous/acetic acid mixtures containing 5×10^{-5} M of dyes at pH 3.5; UV-Vis absorption spectra of DO (red line) and DR (black line) dyes obtained in the same conditions (C).

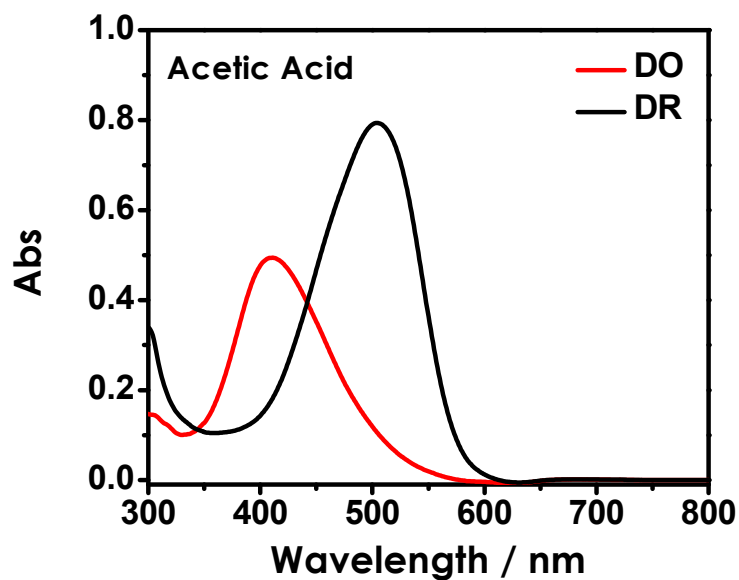


Figure S3: UV-Vis absorption spectra of Disperse Orange (DO, red line) and Disperse Red (DR, black line) dyes at concentration of 5×10^{-5} M in glacial acetic acid.

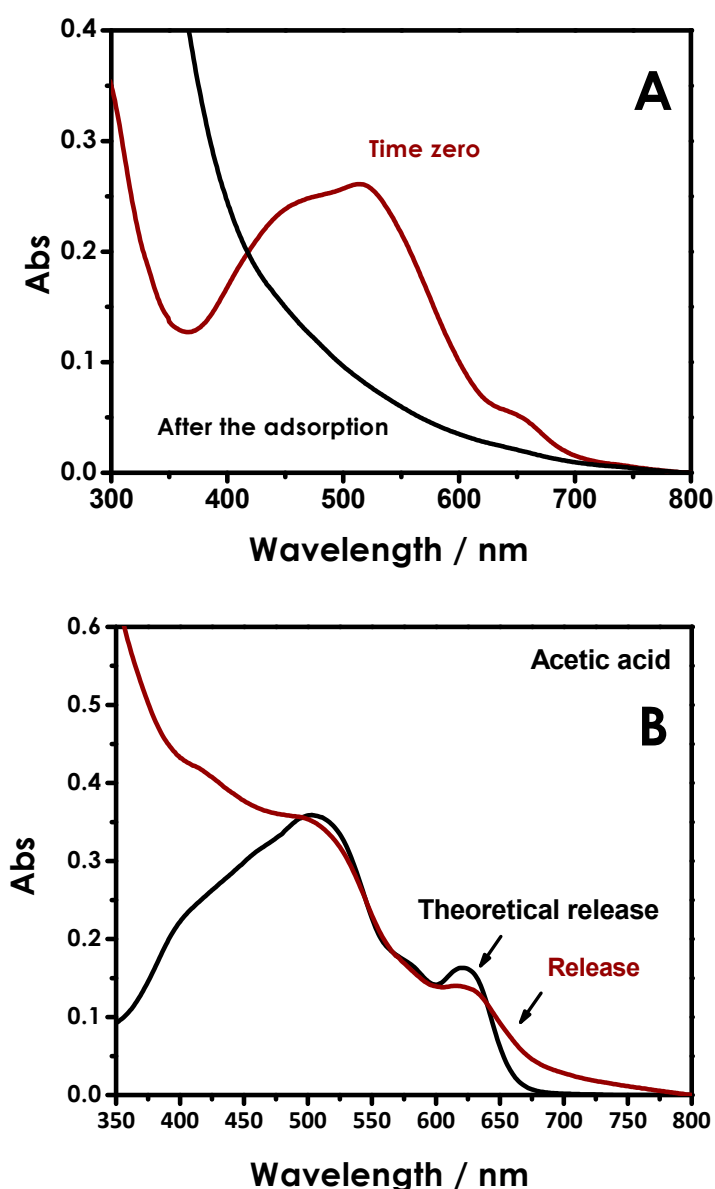


Figure S4: Preliminary results related to the mixture of three disperse dyes: Comparison between Visible absorption spectra obtained for an aqueous solution of Disperse Orange, Disperse Red and Disperse Blue, at pH 7, in the presence of 1 g of olive pomace before and after the adsorption (A); Comparison between Visible absorption spectra obtained in acetic acid after the release of adsorbed Disperse Orange, Disperse Red and Disperse Blue (B).

Effect of pH and preliminary investigation on Direct Blue adsorption by OP_P.

Experiments were performed changing the pH of dye solutions from 3.50 to 6.00 removing the acetic acid. The absence of significant variations related to the adsorption processes (*data not shown*) confirmed the slight role of electrostatic interactions. Gercel et al. [1] and references therein, reached the same results using Disperse Orange 25 and a biomass plant material as biosorbent [1]. The same results were also obtained using Disperse Blue, an anthraquinone dye, and olive pomace [2]. It is worth to mention that although the pH changes the OP_P surface charge, our dyes do not present ionizable groups that could be affected by pH modification, confirming the obtained results. In order to strengthen this hypothesis, a completely different dye respect to DR and DO was used. Direct Blues (dB) was chosen as a model ionic direct dye. **Scheme S1** shows the molecular structure of this dye evidencing the main differences between dB and disperse dyes. Once again the visible band of this

dye was diagnostic to follow the adsorption process (**Figure S5**). The typical absorption band at around 600 nm was observed and explained considering a π - π^* transition having a charge transfer character [2,3]. The same parameters affecting the DO and DR adsorption processes were also investigated.

In particular, **Figure S6A** shows that, increasing the OP_P amount, as already observed for disperse dyes, the contact time for removing dB from water decreased (see the plateau region, indicating the q_t max value). For removing dB in the experimental conditions used for DO and DR, the lowest amount of OP_P (0.50g) required 3 h, while the time increased to 120 minutes for 1.00g of pomace and 30 minutes for 3.00g. These data suggested a different mechanism of interaction involving dB and OP_P. Indeed, disperse dyes were completely removed, after 10 minutes, using 1.00g of OP_P. A similar efficiency was obtained only decreasing the pH of dB solution; at pH 2, the almost complete removal of dB, using 1.00g of OP_P, required 30 minutes. However, it is possible to observe (**Figure S6B**) that, in general, reducing the pH values, the efficiencies of the adsorption process increased. Surprisingly, when basic pH values (for example pH=9) were adopted, the calculated efficiency, compared with results obtained at pH 6, appeared improved. These results indicated the occurrence of pH-dependent electrostatic interactions, involving the sulfonate groups of dB molecules and OP_P [4]. Interesting results were obtained increasing the OP_P/dB solution temperature values. **Figure S6C** reports the obtained results in terms of q_t values. By using 1.00g of OP_P at pH≈6, in water, the contact time for obtaining the almost total dye removal from water decreased from 120 minutes at 25°C to 40 minutes at 80 and 100°C. In particular, at higher temperature the mobility of dyes is expected to increase increasing the diffusion. Additionally, the internal structure of the OP_P could be modified enlarging the pore sizes distribution, enabling the large dye molecules to penetrate into the structure in higher quantities. As observed for DO and DR, also in this case the adsorption process showed an endothermic character. Overall, the obtained results arisen from the study of dB, suggested and confirmed that the kind of interactions when disperse dyes and the pomace are considered were not essentially electrostatic, involving, on the contrary, H-bonds and hydrophobic forces [2].

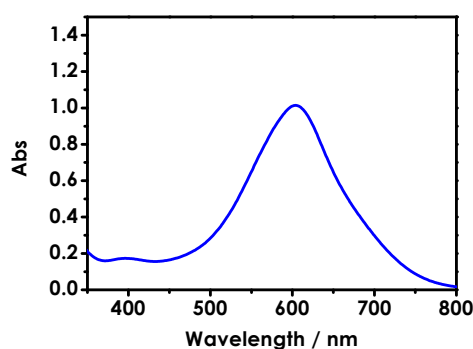


Figure S5: UV-Vis absorption spectra of direct Blue (dB), at concentration of 5×10^{-5} M, in water.

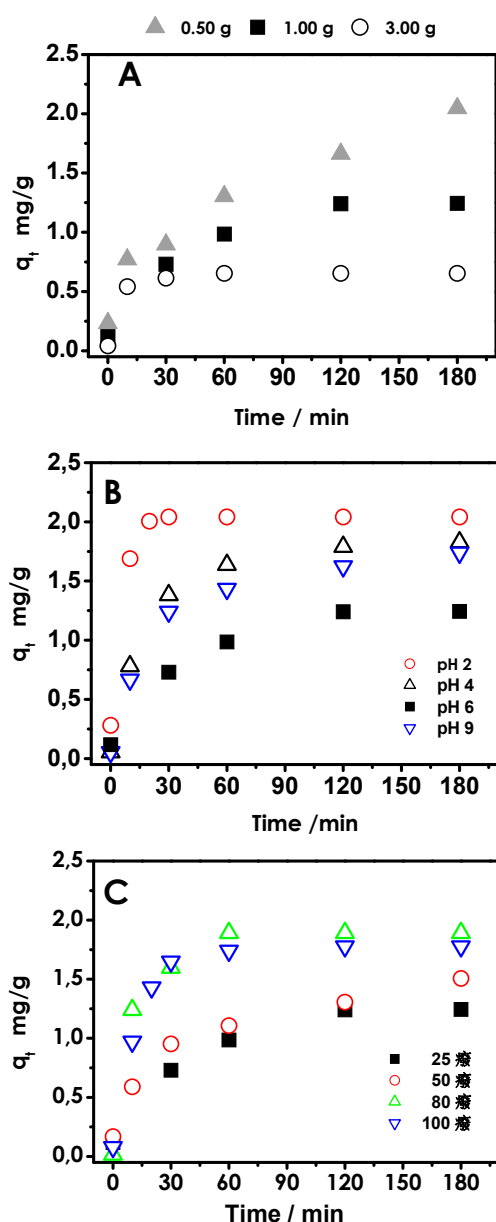


Figure S6: Effect of sieved Olive Pomace, OP_p, a mount (gram for 40 mL of dye solutions) on the adsorption capacity q_t (mg \times g⁻¹) for direct blue, dB, removal from aqueous solutions ($5 \times 10^{-5} \text{ M}$) (A); effect of pH values on the adsorption capacity q_t (mg \times g⁻¹) of dB removal from aqueous ($5 \times 10^{-5} \text{ M}$) solutions, at fixed OP_p amount (1.00 g) (B); effect of temperature values (25, 50, 80 and 100 °C) on the adsorption capacity q_t (mg \times g⁻¹) of dB removal from aqueous ($5 \times 10^{-5} \text{ M}$) solutions, at fixed OP_p amount (1.00 g) (C).

XPS analysis.

In order to draw more detailed information about the adsorption process and to gain insights into the surface chemical composition of OPP before and after the adsorption process, XPS analyses were carried out. Considering the chemical composition of OP, presented in the introduction and mainly consisted of cellulose, lignin, amino acid, protein, uronic acids and polyphenolic compounds the XPS atomic percentages of OP_p and OP_p+DO and OP_p+DR are reported in **Table S1**. In the whole, significant signals were detected at 284.80 eV, 531.90 eV and 399.68 eV. The first signal was attributed to the main presence of C-(C,H) moieties, with the partial contribute at higher Binding Energy of the

C-OH groups, confirmed also by the high percentage of O1s detected at 531.90 eV [2,5]. Even though the hydrocarbon contamination at 284.80 eV cannot be excluded, the main presence of lignin with the contribute of cellulose and/or cellulose-like structures, *i.e.* hemicellulose, could be supposed. The N1s signal at 399.41 eV suggested the presence of amino acids and proteins. Overall, the highest atomic percentage evidenced the main presence of lignin and cellulose [2]. Interestingly, the presence of DO and DR induced variations both in peak positions and atomic percentages. As expected, when DR and DO were adsorbed, the atomic percentage of C1s appeared increased due to the contributions of -CH₂ and -CH₃ moieties and of aromatic carbon atoms in the phenyl residues. In particular, the C1s percentage resulted more significantly affected in the case of DR. In fact, by looking at **Scheme 1**, the DR chemical structure is characterized by the presence of two ester chain (one more than DO), made of carbon atoms, linked to the a nitrogen atom, likely responsible of the higher C1s percentage. About the O1s signals, they appeared shifted towards lower binding energies with a noticeable increase in the percentage area if DR was considered. Additionally, also N1s of OP_P+DO and OP_P+DR changed with important effect on the atomic percentage of OP_P+DR. If the ratio between the peak area percentages of N1s and O1s was considered, a linear decrease was observed from 0.088 to 0.072 and 0.054 in the case of OP_P+DO and DR, respectively. These results suggested a novel arrangement of OP_P components after the dyestuff adsorption, thus proposing interaction involving moieties containing oxygen and amino groups. Moreover, especially in the case of OP_P+DO, the N1s signal occurred shifted to lower Binding Energy value indicating a more probable not protonated amino moiety, once again suggesting the real scarce role of electrostatic interactions between dyes and adsorbent material.

Table S1: XPS surface atomic concentrations of sieved Olive Pomace, OP_P, and OP_P in presence of dyes

	OP _P		OP _P + DO		OP _P + DR	
Signals	BE	[%]	BE	[%]	BE	[%]
C 1s	284.80	68.91	284.80	69.73	284.80	71.46
O 1s	531.90	26.55	531.32	27.50	532.04	26.34
N 1s	399.68	2.34	398.97	1.99	399.58	1.43
Si 2p	101.74	1.14	//	//	//	//
Ca 2p	//	//	347.26	0.78	347.51	0.74

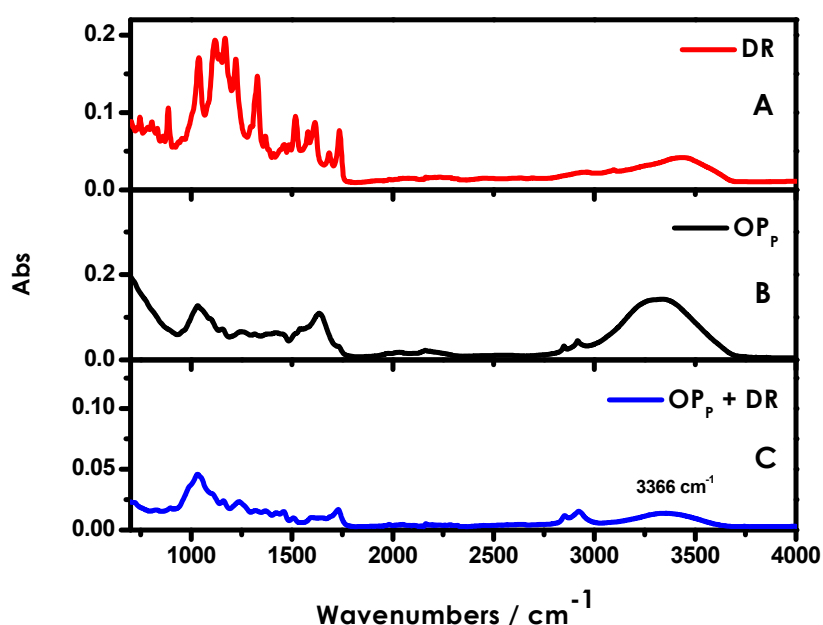


Figure S7: Comparison between detailed views (wavenumbers range: 600–4000 cm^{-1}) of FTIR –ATR spectra of DR (red curve); of sieved olive pomace, OP_r, (black curve) and of OP_r + DR composite material (blue curve).

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