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Mechanism of Alizarin Red S and Methylene Blue Biosorption onto Olive Stone: Isotherm study in Single and Binary Systems

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ABSTRACT

The biosorption process of anionic dye Alizarin Red S (ARS) and cationic dye methylene blue (MB) as a function of contact time, initial concentration and solution pH onto olive stone (OS) biomass has been investigated. Equilibrium biosorption isotherms in single and binary systems and kinetics in batch mode were also examined. The kinetic data of the two dyes were better described by the pseudo second-order model. At low concentration, ARS dye appeared to follow a two-step diffusion process, while MB dye followed a three-step diffusion process. The biosorption experimental data for ARS and MB dyes were well suited to the Redlich-Peterson isotherm. The maximum biosorption of ARS dye, $q_{max} = 16.10 \text{ mg/g}$, was obtained at pH 3.28 and the maximum biosorption of MB dye, $q_{max} = 13.20 \text{ mg/g}$, was observed at basic pH values. In the binary system, it was indicated that the MB dye diffuses firstly inside the biosorbent particle and occupies the biosorption sites forming a monodentate complex and then the ARS dye enters and can only bind to untaken sites; forms a tridentate complex with OS active sites.

Keywords: Anionic Dye; Alizarin Red S; Cationic Dye; Methylene Blue; Dyes Removal; Biosorption; Olive Stone.

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1. Introduction

Large amounts of dye contaminated wastewater are being released yearly from leather, cosmetics, pharmaceutical, plastics and textile industries, and results in an impending hazard to human health and the ecosystem (Cao et al., 2014; Semeraro et al., 2015). The existence of such dyes in receiving water bodies is undesirable as they cut off sunlight and reduce photosynthetic activities of autotrophic organisms (Albadarin et al., 2014). The problem is escalating because these dyes are stable and non-biodegradable (Gorgulu Ari and Celik, 2013); dyes are designed to hold colour on various materials and resist water, soap and oxidizing agents (Khataee et al., 2013). Consequently, the removal of dyes from industrial effluents is a challenging problem and it is essential to optimize dye-removal methods. The low efficiency, high cost, and in some cases, the production of toxic by-products make some physical and chemical approaches such as filtration, coagulation, photocatalytic degradation and advanced oxidation processes impractical and expensive to operate (Kabbout and Taha, 2014). Biosorption has been proven as an effective and cheap process, especially when using biowastes and agricultural by-products as the biosorbent (Albadarin et al., 2011). The search for low-cost and locally available waste materials for the biosorption of dyes continues and, recently, has been extensively accelerated (Abdolali et al., 2014; Guerrero-Coronilla et al., 2015; Guo et al., 2014; Magriotis et al., 2014; Wang et al., 2015). Olive crops cover a global cultivated area of approx. 10 million hectares. One main by-product produced in olive oil extraction and pitted table olive manufacture is olive stone. In Spain during the 2009/2010 season, olive oil and table olives world production result in 0.17 and 2.10 million tons, respectively (The Int. Olive Coun. 2012). This by-product is mainly turned into bioethanol or directly burnt to produce energy (Cuevas et al., 2015; Valentina Hernández et al., 2014). Using raw olive stones as biosorbent is another economic and environmental alternative (Ronda et al., 2013). This offers the olive processing industry an opportunity to make valuable use of the huge quantities of olive stones generated every year. Hence, olives stone (OS) was employed in this study for the biosorption of some dyes. Among the hazardous dyes, Alizarin Red S (ARS) and Methylene Blue (MB) are prime contaminants in the environment, and hence, these were selected as model dye systems. Alizarin Red S is a water soluble anthraquinone dye, is used extensively in the textile industry as a staining agent. It is considered to be one of the most recalcitrant and durable pollutants (Sun et al., 2011). This is due to its complex structures of aromatic rings that afford high optical and physicochemical stability (Fu et al., 2011). Methylene Blue is a cationic thiazine dye commonly used in various industrial applications due to its high adsorption ability. It is not regarded as highly toxic, though, it may cause several harmful effects, such as: difficult breathing on inhalation, gastritis, severe headache, painful micturition, and methemoglobinemia-like syndromes if large amounts are swallowed (Bhattacharyya and Sharma, 2005). The studies dealing with the removal of Alizarin Red S using raw biosorbents are scarce. However, previous studies on the removal of ARS onto activated materials showed that adsorption processes are very promising for pollution control (Fu et al., 2011; Zhang et al., 2001). For instant, a small amount of gold nanoparticles loaded on activated carbon (0.015 g) combined with ultrasound device achieved a high adsorption capacity (123.4 mg/g) in 5 min (Roosta et al., 2014). On the other hand, methylene blue biosorption has been investigated widely though the removal mechanism in binary systems has not yet been clearly understood. The main objectives of this study are to investigate: (i) the chemistry and the mechanism of ARS and MB biosorption onto olive stone and the type of OS-ARS, -MB interfaces occurring; (ii) the biosorption equilibrium and kinetic experimental data required for the design and operation of column reactors; (iii) the simultaneous biosorption isotherm of the two dyes in binary systems.

2. Materials and Methods

2.1. Olive stone (OS) biomass

The olive stones were crushed and 1000–355 μ m fraction was chosen for the characterization

and biosorption experiments without any pre-treatment. The biomass was washed a number of times with boiled water and finally with distilled water to remove any adhering dirt, and dried at 110 °C for 24 hrs. Full and comprehensive characterization of OS can be found in a previous investigation (Blázquez et al., 2014). However, fourier transform infrared spectroscopy and scanning electron microscopy were employed to characterize the OS before and after ARS and MB biosorption. The FT-IR analyses for olive stones surfaces before and after ARS and MB biosorption were tested using the KBr pressed disc technique using a Perkin Elmer Spectrum 100 within the range of 400–4000 cm⁻¹. For the SEM analysis, OS samples were coated with gold and vacuumed (5–10 min) for electron reflection prior to analysis on a JEOL-JSM 6400 scanning microscope. The samples used for the FT-IR and SEM analysis were collected from the pH effect experiment (optimum pH).

2.2. Procedures

Alizarin Red S (342.2 g/mol) and Methylene Blue (319.8 g/mol) were purchased from Sigma Aldrich, UK. All chemical reagents were of analytical grades. Synthetic dye solutions used in the experiments were prepared with distilled water (resistivity 18.24 Ω cm). Concentrations were measured using a UV–VIS spectrophotometer (Perkin Elmer LAMBDA 25, UK) at a maximum wavelength $\lambda_{max} = 668$ nm for MB (Albadarin et al., 2014). Measurement of ARS concentration was carried out at $\lambda_{max} = 425-514$ nm (Roosta et al., 2014) to minimize the pH effect on ARS concentration determination. It is known that, depending on the isosbestic point, ARS will change colour i.e. pale yellow at pH = 2; yellow orange at pH = 3–4.9; red at pH = 6.2–9 and violet at pH = 11 (Olivier Thomas and Burgess, 2007). The experiments of ARS and MB biosorption from aqueous solutions were carried out in a series of 50 cm³ glass jars; samples were regularly shaken (mechanical shaker, GerhardT type LS 5) at 100 rpm and 20 °C for 72 hrs to ensure reaching the equilibrium. The effect of initial solution pH on the removal of ARS and MB was examined in the range of 2–9, containing 25 cm³ of dye solution with *C*₀ of 110

mg/dm³ and biomass dosage of 5.0 g/dm³. The pH was altered using 0.1 M HCl or 0.1 M NaOH. The same procedures were employed to investigate the effect of contact time and biosorption isotherms. The initial concentrations ranging from 30 to 205 mg/dm³ for ARS and MB were employed for the contact time experiment. For the biosorption isotherm studies in single and binary systems, $C_0 = 5-105$ mg/dm³ for ARS and MB were used. The isotherm studies in binary system were investigated at pH 3.4 and 7.2. ARS and MB uptake, *q* (mg/g), and percentage of removal (%) were calculated according to Eq. (1) and (2), respectively:

$$q = \left[\frac{C_o - C_e}{M}\right] \times V \tag{1}$$

The percentage removal = $\left[1 - \frac{C_e}{C_o}\right] \times 100\%$ (2)

where C_0 and C_e are the initial and equilibrium concentrations of ARS and MB in mg/dm³, *M* is the amount of dry biomass in grams and *V* is the volume of the ARS/MB solution in dm³.

3. Results and Discussion

3.1. Effect of contact time and initial dye concentration

The effect of contact time on the biosorption capacity of OS for ARS and MB was studied at

five different initial dye concentrations as revealed in Table 1. As expected, the biosorption capacity of OS increased with an increase in the initial dye concentrations. The ARS removal decreased from 85% to 50% as the ARS concentration was increased from 32 to 190 mg/dm³. While the MB removal decreased from 75% to 40% when the dye concentration increased from 30 to 205 mg/dm³. Figure 1 shows that the biosorption at various concentrations is fast in the initial stages and steadily decreases with the progress of biosorption until the equilibrium is reached. The difference in the biosorbed concentration of ARS and MB at equilibrium (q_e) and at time t (q_t) provides the key driving force to overcome all mass transfer resistances of the dye between the aqueous and solid phases (Liao et al., 2012).

3.2. Kinetic modelling

In the current study, the pseudo first-order model (Lagergren, 1898), pseudo second-order model (Ho and McKay, 1999), Intraparticle diffusion model (Weber and Morris, 1963) and Boyd kinetic model (Boyd et al., 1947a) were tested.

3.2.1. Pseudo first- and second-order kinetic models The pseudo first-order model equation is given as follow:

$$q_t = q_e \left(1 - e^{-k_1 t} \right) \tag{3}$$

The pseudo second-order equation is given as;

$$q_{t} = \frac{k_{2}q_{e}^{2}}{\left(1 + k_{2}q_{e}t\right)}t$$
(4)

where k_1 (1/min) and k_2 (g/mg min) are the rate constants for first- and second-order models. Table 1 summarizes the parameters of the pseudo first- and second-order kinetic models for ARS and MB biosorption onto OS. The highest R^2 values and well closer calculated $q_{e,cal}$ to those acquired by experiments, $q_{e,exp}$, confirmed that the biosorption process for both dyes is best described by the pseudo-second-order equation (Figure 1). The above conclusion reveals that the biosorption is a chemical process and the dye uptake capacity is proportional to the number of active sites (Glocheux et al., 2013; Weifeng Liu et al., 2011). Also, in Table 1, the nonlinear relations between the initial concentrations, C_0 , of the dye and the rate constant, k_1 , implies that mechanisms such as ion exchange and chelation are involved in the biosorption process. The decrease in rate constant, k_2 , of the second-order model is attributable to the competition between higher levels of dye molecules (Albadarin et al., 2012; Albadarin et al., 2014).

1 3.2.2. Intraparticle diffusion model

The intraparticle diffusion model was employed in order to distinguish the different resistances
to diffusion of ARS and MB onto olive stone. The model links the pollutant adsorbed at a given
time with the time *t* following the Equation (5):

5
$$q_t = k_{di} t^{0.5} + C_{di}$$
 (5)

6 k_{di} , the intraparticle diffusion rate is constant and expressed in mg/g.h^{0.5} where *i* represents the 7 diffusion phase number; C_{di} is proportional to the boundary layer thickness.

8 It can be seen in Table 2 that MB diffuses faster than ARS at low and high concentration. The plot of q_t versus $t^{0.5}$ is linear when the intraparticle diffusion is the main resistance step in the 9 10 experimental conditions. In this study, several regions were observed for the diffusion of ARS 11 and MB in the porous olive stone materials; none of the plots passed through the origin ($C_{di} \neq$ 0) (see supplementary data: SD1). The values of intercept increased when the initial dye 12 13 concentration was increased; C_{di} values give an idea about the boundary layer thickness; the larger the 14 intercept, the greater is the boundary layer effect (values not shown here). The presence of different linear regions in the plot of q_t versus $t^{0.5}$ implies that the intraparticles diffusion is not the only 15 16 operative mechanism and that the biosorption kinetics of dyes on OS was controlled by both 17 surface and intraparticle diffusion processes. At low concentration, the difference is more 18 obvious and MB followed a three-step diffusion process while ARS seems to follow a two-step 19 diffusion process. The difference in diffusion steps may be related to the molecular mass i.e. 20 the higher the molecular mass, the slower the rate of diffusion. The higher charge density of 21 MB compared to ARS enables a faster diffusion in OS biomass. In terms of diffusion 22 parameters, the difference between ARS and MB biosorption is clearly observed for the first 23 intraparticle diffusion step. The diffusion coefficients for MB biosorption are more than double those for ARS biosorption (Table 2). The correlating coefficients, R^2 , reported in Table 2 for 24 the intraparticle diffusion kinetic model are generally lower than that of the pseudo second-25

order kinetic for the biosorption of ARS and MB onto OS. These findings further confirm that
the pseudo second-order mechanism is dominant and the overall rate of biosorption process is
controlled by several portions.

29 3.2.3. Boyd kinetic model

The Boyd kinetic model was employed to confirm the actual rate-controlling step involved in the ARS and MB biosorption onto the OS. The Boyd kinetic equations are defined as (Boyd et al., 1947b):

33
$$F = 1 - \left(\frac{6}{\pi^2}\right) \exp(-Bt);$$
 where $F = q_t/q_e$ (6)

$$34 \qquad B \times t = -0.4977 - \ln(1 - F) \tag{7}$$

35 If a plot Bt versus t is a straight line passing through the origin, it indicates a particle diffusion 36 mechanism; contrarily, film-diffusion or chemical reaction control the adsorption rate. The 37 plots (not shown here) revealed that the experimental data for both dyes do not follow the Boyd model and therefore particle diffusion does not control the rate of the biosorption process. Once 38 39 again, this suggests that film-diffusion or chemical reaction controls the rate of biosorption. 40 The biosorption systems were, in general, controlled by chemisorption including valence forces 41 as covalent bonds/ion exchange between the adsorbent and dye molecules until the surface 42 active sites were fully occupied. After that, dye molecules diffused into the biosorbent for 43 further interactions (Tavlieva et al., 2013).

44 3.3. pH effect

The solution pH plays a significant role in the chemistry of both the OS biomass and dye molecules, and has a major effect on electrostatic charges that are imparted by ionized dye molecules. As illustrated in Figure 2, the removal of ARS and MB from aqueous solution is greatly dependent on the pH of the solution, and various functional groups such as hydroxyl, carbonyl and amine groups distributed on the surface of OS were affected by the solution pH 50 (Blázquez et al., 2014). At pH above 5, the amount of ARS biosorption decreases noticeably 51 following a typical anionic adsorption behaviour (Silvina Pirillo et al., 2009). For the anionic 52 dye, ARS, the adsorption capacity decreased from 14.31 to 0.662 mg/g when the pH increased 53 from 3.28 to 8.16. This is predominantly attributed to the deprotonation of the biosorbent 54 surface and the presence of excess OH⁻ ions competing with ARS molecules, which exist 55 mainly in a monoanionic form (Olivier Thomas and Burgess, 2007). On the other hand, 56 opposite trends were observed for cationic dye, MB. The amount of MB biosorbed increased 57 with an increase in the pH of the MB solution; the maximum adsorption capacity of MB was 58 11.35 mg/g, observed at pH 7.2. The point of zero charge of the olive stone biomass has been 59 previously determined as 5.17 (Ronda et al., 2013). Therefore, these trends could also be well 60 explained by the electrostatic interaction between the negatively charged surfaces of the 61 biosorbent, at $pH > pH_{PZC}$, and the cationic dye (Galán et al., 2013). The results are in 62 agreement with previous studies in which maximum biosorption of anionic dyes were observed 63 at pH below 5, and the optimal removal of cationic dyes reported at basic pH values (Peng et 64 al., 2014). It is worth noting that during/after dyes biosorption, the pH of the dye solution changed and this is a strong indication of a dye-hydrogen ion exchange and complexation 65 66 processes. The amount of dye biosorbed, mmol/g, was calculated and compared to the number of H+ ions released/adsorbed. The molar ratio of the biosorbed dye to released/adsorbed H+ 67 68 ions was 2.926 and 1.014 for ARS and MB, respectively.

69 3.4. Isotherm experiments

70 3.4.1. Single systems

Figure 3 shows the equilibrium isotherms of ARS and MB dyes onto OS biosorbent. Langmuir, Freundlich, Redlich-Peterson and Temkin isotherms were applied to the experimental data using non-linear regression in SigmaPlot Version 11 and the summary of the fits is presented in Table 3. The data demonstrates that the Langmuir ($R^2 = 0.995$) isotherm is the best model 75 for describing the biosorption of MB onto OS. For the ARS and MB dye, the Redlich-Peterson isotherm ($R^2 = 0.994$ and $R^2 = 0.998$) gives the best description of the experimental data 76 77 (Temkin and Levich, 1946). For MB biosorption, the value of β obtained using the Redlich-78 Peterson isotherm was close to unity (1.101), indicating that the isotherm is approaching the 79 Langmuir rather than the Freundlich isotherm from (Redlich and Peterson, 1959). Also, the 80 good fit of MB experimental equilibrium data to the Langmuir isotherm indicates the monolayer coverage and chemisorption of MB onto OS. According to Table 3, the olive stone 81 82 has the monolayer Langmuir biosorption capacities of 16.10 and 13.20 mg/g for ARS and MB, 83 respectively. At the high C_0 values used in this study, ion exchange sites and functional groups 84 are more significant than the surface area (0.16 m^2/g (Blázquez et al., 2014)) for biosorption, 85 where chemical precipitation of the dye anions/ cations may play a dominant role in the dye 86 removal. This may explain the high biosorption capacities despite the relatively small surface 87 area of OS. The value of 1/n obtained from the Freundlich isotherm for ARS was 0.457 and 88 0.426 for MB, which shows that the biosorption of ARS and MB onto OS is favourable 89 (Albadarin et al., 2012). The slightly higher value of $K_{\rm F}$ for ARS dye indicates that OS 90 possesses a higher biosorption capacity for ARS compared to MB dye. Table 4 provides a 91 comparison between the biosorption capacities of ARS and MB dyes with earlier studies (Ai et 92 al., 2011; Albadarin et al., 2014; Banat et al., 2003; Fu et al., 2011; Ghaedi et al., 2011; Gürses 93 et al., 2006; Janoš et al., 2003; Wu et al., 2004). Keeping in mind that the olive stone used here 94 is cheap, was used without any treatment and required very little preparation, the biosorption 95 capacities for ARS and MB onto OS are very similar to those of alternative materials from earlier investigations. 96

97 3.4.2. Binary systems

98 The ARS and MB dyes used in this study have very similar isotherms; ARS and MB structures 99 contain three benzene rings in a linear structure with no side chain. Ignoring the molecular charge, this suggests that in the case of competitive biosorption between the dyes, the process
can be considered as a single-component biosorption of a pseudo-component with properties
between the properties of the real components (Wouter Delée et al., 1998). Hence, the next
step of the present work was to discuss the simultaneous biosorption isotherm of two dyes at
their optimum pH (3.4 and 7.2).

105 The amount of dye biosorbed was determined and compared to that for the single system so as 106 to investigate the competitive character of the interaction between the two dyes. In Figure 4, 107 the curve for the binary dye solution at pH = 7.2 is almost identical to the sum of the curves for 108 the single-components. The above observations reveal that there is very limited competition 109 between the two components examined here. However, this competition can be detected and 110 this explains why the total adsorbed quantity of single-dyes is larger than a mixture of the two 111 components with the same concentration. This demonstrates that there is an abundant number 112 of active sites by which the two dyes can be sequestrated and for which they will, to some 113 extent, compete for if co-existing in a multicomponent systems.

114 Furthermore, it can be concluded that when in the binary system (pH = 7.2), the MB dye is first 115 to penetrate the biosorbent particle and to occupy the biosorption sites. Then, the ARS dye 116 enters and can only bind to untaken sites in an irreversible equilibrium scenario (George Z. 117 Kyzas et al., 2013) (Figure 4). If the above assumption is correct, the MB positive molecules 118 may influence the biosorption of ARS negative molecules by providing a positively charged 119 phase and consequently decreasing the repulsion between the ARS molecules and enhance the 120 biosorption affinity. The binary system at pH = 3.4 seems to lower the amount of dyes 121 biosorbed. This can be due to the high completion between the hydrogen ions and the MB 122 molecules. However, this needs further investigation and will be considered for future work.

123 3.5. FT-IR and SEM analysis

124 Olive stone is a lignocellulosic material, with hemicellulose, cellulose and lignin as main

125 components. The FT-IR spectrum for OS biomass in Figure 5 is very similar to those reported 126 for other biomasses such as tea waste and date stone (Albadarin et al., 2013). Peaks were detected around 3430 and 2920 cm⁻¹ and can be attributed to -NH₂, -OH groups and -CH 127 stretching, respectively. Whereas >C=O stretching vibration, symmetric bending of CH₃, – 128 OCH₃ in ethers, secondary amine group, esters such as CH₃-CO-O- and -SO₃ of 129 hemicelluloses were observed between 1750 and 1047 cm⁻¹. The FT-IR spectra in Figure 6 130 shows changes in surface properties and functional groups of the OS biomass after the 131 132 biosorption of ARS and MB, confirmed by the change in the peak heights and shifts of 133 functional group bands due to dyes biosorption.

134 The difference in the absorbance reading from 1 hour to 72 hours, although negative for ARS 135 but positive for MB, is very similar, indicating that almost the same number of dye molecules 136 are attached to the olive stone surface. The shifts and shape-changes occurring in the -OH 137 stretching band at 3430 cm⁻¹ shows that the dye is attached to the oxygen atoms creating 138 monodentate, bidentate or tridentate bonds and replacing the water molecules (Benjamin and 139 Leckie, 1981). This conclusion is in agreement with the previous findings for the molar ratio 140 between the biosorbed dye and H⁺ released or adsorbed in section 3.3 and confirms that ARS 141 formed a tridentate complex whereas MB formed a monodentate complex with OS sites.

The topography of the olive stone before and after biosorption of ARS and MB are shown in Figure 6. It is clear that the OS surface is non-homogeneous and rough with some visible pores and fibre-like structures. These surface characteristics will provide an increase in the uptake capacity of dye solution. After the biosorption of ARS and MB dyes, the OS surface is smoother indicating that the dyes were densely and homogeneously adhered to the surface of OS.

148 **4.** Conclusions

149 Raw biomass of olive stones was proven useful for biosorption of Alizarin Red S and

150 Methylene Blue dyes. The biosorption reactions were shown to be dependent on pH, initial dye

151 concentration and contact time. The kinetic of the biosorption process was well described by

152 the pseudo-second order model. From the diffusion models, it was concluded that film-

153 diffusion or chemical reaction controls the rate of biosorption. Process mechanisms, namely

- 154 ion exchange and chelation, were involved in the biosorption. ARS maximum capacity was
- found at pH = 2, whereas MB maximum capacity was obtained at pH = 7.2. it can be concluded
- 156 that ARS and MB formed tridentate and monodentate complexes, respectively, with OS sites.
- 157 FT-IR analysis confirmed the interactions between olive stone biosorbent surface and ARS and
- 158 MB dye molecules.

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Figure 1: The fitting of pseudo first- (continuous line), second-order (short-dash line) models.

Figure 2: Biosorption of Alizarin Red S (ARS) and Methylene Blue (MB) onto olives stone as a function of pH. Experimental conditions: $C_0 = 110 \text{ mg/dm}^3$; volume 25 cm³; biosorbent dosage 5.0 g/dm³; and shaking speed 100 rpm for 72 hrs.



Equilibrium concentration (mg/dm³)



Equilibrium concentration (mg/dm³)

Figure 3: Non-linear forms of biosorption isotherm plots for ARS and MB biosorption onto OS.



Equilibrium concentration (mg/dm³)



Irreversible equilibrium scenario: ARS molecules can be bound only to unoccupied sites



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- Figure 4: Comparison between total $C_e vs$ total q_e at various pH for ARS and MB biosorption in single and binary mixture: ($q_e = q_{e,ARS} + q_{e,MB}$) and ($C_e = C_{e,ARS} + C_{e,MB}$) and proposed irreversible equilibrium scenario for the biosorption of ARS and MB onto OS in binary system.



Wavenumber (1/cm)



Figure 5: Fourier transform infrared (FT-IR) spectroscopy spectra of -unloaded olive stone (OS) and Alizarin Red S- (ARS-OS) and Methylene Blue-loaded olive stone (MB–OS).



332 Figure 6: Scanning electron microscopy of unloaded olive stone and ARS- and MB-loaded olive stone.

q _{essip} (mg/g) q _{ecal} (mg/g) k ₁ R ² q _{ecal} (mg/g) k ₂ R ² 32 (mg/dm ³) 5.531 5.008 0.008 0.987 5.363 1.80 × 10 ³ 0.992 53 (mg/dm ³) 8.942 7.669 0.007 0.819 8.030 1.70 × 10 ³ 0.910 4RS 87 (mg/dm ³) 13.66 12.15 0.008 0.973 13.14 0.90 × 10 ³ 0.986 125 (mg/dm ³) 15.81 15.00 0.004 0.991 16.21 0.40 × 10 ³ 0.997 190 (mg/dm ³) 19.06 17.61 0.009 0.959 18.78 0.30 × 10 ³ 0.986 29 (mg/dm ³) 8.750 7.588 0.117 0.967 7.938 0.021 0.978 95 (mg/dm ³) 13.01 12.77 0.094 0.990 13.33 0.001 0.996 205 (mg/dm ³) 16.30 15.43 0.059 0.974 16.50 0.001 0.975		Co		Pseudo first-order model			Pseudo second-order model		
(mg/g) (mg/g) (1/min) (mg/g) (g/m min) 32 (mg/dm³) 5.531 5.008 0.008 0.987 5.363 1.80 × 10³ 0.992 53 (mg/dm³) 8.942 7.669 0.007 0.819 8.030 1.70 × 10³ 0.910 87 (mg/dm³) 13.66 12.15 0.008 0.973 13.14 0.90 × 10³ 0.986 125 (mg/dm³) 15.81 15.00 0.004 0.991 16.21 0.40 × 10³ 0.997 190 (mg/dm³) 19.06 17.61 0.009 0.959 18.78 0.30 × 10³ 0.986 29 (mg/dm³) 4.381 3.878 0.074 0.974 4.117 0.023 0.982 60 (mg/dm³) 8.750 7.588 0.117 0.967 7.938 0.021 0.978 95 (mg/dm³) 13.01 12.77 0.094 0.990 13.33 0.001 0.975 205 (mg/dm³) 16.30 15.43 0.059 0.974 16.50 0.001 0.975			$q_{ m e,exp}$	$q_{ m e,cal}$	k_1	R^2	$q_{ m e,cal}$	k_2	R^2
32 (mg/dm ³) 5.531 5.008 0.008 0.987 5.363 1.80 × 10 ³ 0.992 53 (mg/dm ³) 8.942 7.669 0.007 0.819 8.030 1.70 × 10 ³ 0.910 87 (mg/dm ³) 13.66 12.15 0.008 0.973 13.14 0.90 × 10 ³ 0.986 125 (mg/dm ³) 15.81 15.00 0.004 0.991 16.21 0.40 × 10 ³ 0.997 190 (mg/dm ³) 19.06 17.61 0.009 0.959 18.78 0.30 × 10 ³ 0.986 29 (mg/dm ³) 4.381 3.878 0.074 0.974 4.117 0.023 0.982 60 (mg/dm ³) 8.750 7.588 0.117 0.967 7.938 0.021 0.978 95 (mg/dm ³) 13.01 12.77 0.094 0.990 13.33 0.001 0.996 205 (mg/dm ³) 16.30 15.43 0.059 0.974 16.50 0.001 0.975			(mg/g)	(mg/g)	(1/min)		(mg/g)	(g/mg min)	
ARS 53 (mg/dm ³) 8.942 7.669 0.007 0.819 8.030 1.70 × 10 ³ 0.910 ARS 87 (mg/dm ³) 13.66 12.15 0.008 0.973 13.14 0.90 × 10 ³ 0.986 125 (mg/dm ³) 15.81 15.00 0.004 0.991 16.21 0.40 × 10 ³ 0.997 190 (mg/dm ³) 19.06 17.61 0.009 0.959 18.78 0.30 × 10 ³ 0.986 Q (mg/dm ³) 4.381 3.878 0.074 0.974 4.117 0.023 0.982 60 (mg/dm ³) 8.750 7.588 0.117 0.967 7.938 0.021 0.978 95 (mg/dm ³) 13.01 12.77 0.094 0.990 13.33 0.001 0.975 205 (mg/dm ³) 16.30 15.43 0.059 0.974 16.50 0.001 0.975		32 (mg/dm ³)	5.531	5.008	0.008	0.987	5.363	$1.80 imes 10^3$	0.992
ARS 87 (mg/dm³) 13.66 12.15 0.008 0.973 13.14 0.90 × 10 ³ 0.986 125 (mg/dm³) 15.81 15.00 0.004 0.991 16.21 0.40 × 10 ³ 0.997 190 (mg/dm³) 19.06 17.61 0.009 0.959 18.78 0.30 × 10 ³ 0.986 29 (mg/dm³) 4.381 3.878 0.074 0.974 4.117 0.023 0.982 60 (mg/dm³) 8.750 7.588 0.117 0.967 7.938 0.021 0.978 95 (mg/dm³) 11.70 10.26 0.053 0.970 11.03 0.006 0.991 137 (mg/dm³) 13.01 12.77 0.094 0.990 13.33 0.001 0.975 205 (mg/dm³) 16.30 15.43 0.059 0.974 16.50 0.001 0.975		53 (mg/dm ³)	8.942	7.669	0.007	0.819	8.030	$1.70 imes 10^3$	0.910
125 (mg/dm³) 15.81 15.00 0.004 0.991 16.21 0.40 × 10³ 0.997 190 (mg/dm³) 19.06 17.61 0.009 0.959 18.78 0.30 × 10³ 0.986 29 (mg/dm³) 4.381 3.878 0.074 0.974 4.117 0.023 0.982 60 (mg/dm³) 8.750 7.588 0.117 0.967 7.938 0.021 0.978 95 (mg/dm³) 11.70 10.26 0.053 0.970 11.03 0.006 0.991 137 (mg/dm³) 13.01 12.77 0.094 0.990 13.33 0.001 0.975 205 (mg/dm³) 16.30 15.43 0.059 0.974 16.50 0.001 0.975	ARS	87 (mg/dm ³)	13.66	12.15	0.008	0.973	13.14	$0.90 imes 10^3$	0.986
190 (mg/dm³) 19.06 17.61 0.009 0.959 18.78 0.30 × 10 ³ 0.986 29 (mg/dm³) 4.381 3.878 0.074 0.974 4.117 0.023 0.982 60 (mg/dm³) 8.750 7.588 0.117 0.967 7.938 0.021 0.978 95 (mg/dm³) 11.70 10.26 0.053 0.970 11.03 0.006 0.991 137 (mg/dm³) 13.01 12.77 0.094 0.990 13.33 0.001 0.996 205 (mg/dm³) 16.30 15.43 0.059 0.974 16.50 0.001 0.975		125 (mg/dm ³)	15.81	15.00	0.004	0.991	16.21	$0.40 imes 10^3$	0.997
29 (mg/dm³) 4.381 3.878 0.074 0.974 4.117 0.023 0.982 60 (mg/dm³) 8.750 7.588 0.117 0.967 7.938 0.021 0.978 95 (mg/dm³) 11.70 10.26 0.053 0.970 11.03 0.006 0.991 137 (mg/dm³) 13.01 12.77 0.094 0.990 13.33 0.001 0.975 205 (mg/dm³) 16.30 15.43 0.059 0.974 16.50 0.001 0.975		190 (mg/dm ³)	19.06	17.61	0.009	0.959	18.78	$0.30 imes 10^3$	0.986
60 (mg/dm³) 8.750 7.588 0.117 0.967 7.938 0.021 0.978 95 (mg/dm³) 11.70 10.26 0.053 0.970 11.03 0.006 0.991 137 (mg/dm³) 13.01 12.77 0.094 0.990 13.33 0.001 0.996 205 (mg/dm³) 16.30 15.43 0.059 0.974 16.50 0.001 0.975		29 (mg/dm ³)	4.381	3.878	0.074	0.974	4.117	0.023	0.982
MB 95 (mg/dm³) 11.70 10.26 0.053 0.970 11.03 0.006 0.991 137 (mg/dm³) 13.01 12.77 0.094 0.990 13.33 0.001 0.996 205 (mg/dm³) 16.30 15.43 0.059 0.974 16.50 0.001 0.975		60 (mg/dm ³)	8.750	7.588	0.117	0.967	7.938	0.021	0.978
137 (mg/dm³) 13.01 12.77 0.094 0.990 13.33 0.001 0.996 205 (mg/dm³) 16.30 15.43 0.059 0.974 16.50 0.001 0.975	MB	95 (mg/dm ³)	11.70	10.26	0.053	0.970	11.03	0.006	0.991
205 (mg/dm³) 16.30 15.43 0.059 0.974 16.50 0.001 0.975		137 (mg/dm ³)	13.01	12.77	0.094	0.990	13.33	0.001	0.996
		205 (mg/dm ³)	16.30	15.43	0.059	0.974	16.50	0.001	0.975

Table 1: Pseudo first-order and pseudo second-order model constants for ARS and MBbiosorption onto olive stone.

Co		Intraparticle diffusion coefficients in mg/g.h ^{0.5}						
		k _{d1}	R^2	k _{d2}	R^2	k _{d3}	R^2	
	32 (mg/dm ³)	0.280	0.990	0.017	0.671	_	_	
	53 (mg/dm ³)	0.159	0.870	0.025	0.971	_	_	
ARS	87 (mg/dm ³)	0.802	0.963	0.054	0.960	_	_	
	125 (mg/dm ³)	0.557	0.892	0.703	0.979	0.046	0.868	
	190 (mg/dm ³)	2.969	0.874	0.697	0.981	0.031	0.727	
MB	29 (mg/dm ³)	1.039	0.979	0.046	0.893	0.003	0.991	
	60 (mg/dm ³)	2.224	0.990	0.089	0.973	0.051	1.000	
	95 (mg/dm ³)	1.315	0.953	0.193	0.777	0.070	0.907	
	137 (mg/dm ³)	4.353	0.987	0.883	0.990	0.013	0.510	
	205 (mg/dm ³)	0.463	1.000	10.09	0.982	0.118	0.606	

349 Table 2: Intraparticle diffusion model parameters for the different diffusion phase

361	Table 3:	The	Langmuir,	Freundlich,	Redlich-Peterson	and	Temkin	parameters	and	correlation
362	coefficie	nts for	ARS and M	IB dyes bioso	orption onto olive s	tone.				

Model	Parameters	ARS	MB
Langmuir isotherm	$q_{\rm max}$ (mg/g)	16.10	13.20
$q_{\perp} = \frac{q_{\max}bC_e}{d_{\max}bC_e}$	<i>b</i> (dm ³ /mg)	0.112	0.115
$1 + bC_e$	$R_{ m adj}^2$	0.988	0.995
Freundlich isotherm	$K_F ({ m mg/g}({ m dm}^3/{ m mg})^{1/n})$	2.529	2.262
$q_e = K_F C_e^{1/n}$	1/n	0.457	0.426
	$R_{ m adj}{}^2$	0.944	0.959
Redlich-Peterson isotherm	K_R (dm ³ /mg)	1.273	1.306
$a = \frac{K_R C_e}{K_R C_e}$	$a_R \left((\mathrm{dm}^3/\mathrm{mg})^{1/\beta} \right)$	0.016	0.063
$1_e 1 + a_R C_e^{\beta}$	В	1.407	1.101
	$R_{ m adj}{}^2$	0.994	0.998
Temkin isotherm	$A_{\rm T}$ (dm ³ /g)	1.163	1.342
$a = \frac{RT}{\ln A} \ln A$	b_{T}	706.7	899.3
$q_e = b_T$	$R_{ m adj}{}^2$	0.992	0.995

371 Table 4: Comparison of Langmuir biosorption capacities of ARS and MB with results from previous

372 studies.

Material	Ad	lsorbate	Reference		
	ARS [mg/g]	MB [mg/g]			
Olive Stone	16.01	13.20	This work		
Teawaste & Dolomite	_	150.0	(Albadarin et al., 2014)		
Clay	_	58.20	(Gürses et al., 2006)		
Activated clay modified	32.70	_	(Fu et al., 2011)		
by iron oxide					
Silica		11.21	(Janoš et al., 2003)		
M-MCCNT		48.08	(Ai et al., 2011)		
MMT/CoFe ₂ O ₄		97.75	(Ai et al., 2011)		
composite					
Raw date pits		27.27	(Banat et al., 2003)		
Activate Date pits		80.29	(Banat et al., 2003)		
Porous Xerogels	8.30 mmol/kg	_	(Wu et al., 2004)		
MWCNT	161.3	_	(Ghaedi et al., 2011)		

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Time^{0.5} (min^{0.5})

-	
27	70
	19
-	

Figure S1: Intraparticle diffusion model (time^{0.5} vs q_e plots) for ARS and MB biosorption onto OS.