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Magnetically modified *Posidonia oceanica* biomass as an adsorbent for organic dyes removal

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Abstract

Magnetically modified *Posidonia oceanica* sea grass dead biomass was employed as an adsorbent of organic dyes. The adsorption of seven water-soluble organic dyes was characterized using Langmuir adsorption model. The highest calculated maximum adsorption capacity was found for Bismarck brown Y (233.5 mg g⁻¹), while the lowest capacity value was obtained for safranin O (88.1 mg g⁻¹). The adsorption processes followed the pseudo-second-order kinetic model and the thermodynamic studies indicated spontaneous and endothermic adsorption.

Keywords: *Posidonia oceanica*, Neptune balls, magnetic biomass, organic dyes, adsorbent.

Introduction

Posidonia oceanica (L.) Delile is a widely distributed, fast-growing sea grass playing important ecological roles in the Mediterranean ecosystem. The *P. oceanica* dead leaves in the form of so called “Neptune balls” (Fig. 1) are accumulated in a large scale on the beaches. This material is usually collected from the beaches as a waste because of their bad view and also distinctive odour. The collected dead leaves are usually burned to get beaches clean. However, this material contains ca 30% of cellulose and 29% of lignin with many functional groups, such as hydroxyl, sulphonyl, carbonyl and phenolic, that can be effectively used for adsorption purposes (Aydin *et al.*, 2012; Cengiz & Cavas, 2010; Chadlia *et al.*, 2009).

Waste *Posidonia* biomass has recently been tested as a sorbent for the removal of various organic dyes from water solutions. This adsorbent exhibited high maximum adsorption capacity (119.05 mg g⁻¹) towards methyl violet at 45 °C. Pseudo-second-order kinetic model fitted well the experimental data. Negative values of Gibbs free energy implied that the process was spontaneous (Cengiz & Cavas, 2010). Some other dyes were also adsorbed well on the *Posidonia* biomass, as shown by relatively high maximum adsorption capacities; Astrazon red (68.97 mg g⁻¹, Cengiz *et al.*, 2012, Acid yellow 59 (76.9 mg g⁻¹; (Guezguez *et al.*, 2009)), Alpacide yellow (15.11 mg g⁻¹; (Ncibi *et al.*, 2009)) and Reactive red 228 (5.74 mg g⁻¹; (Ncibi *et al.*, 2007)) can serve as examples.

Magnetically modified adsorbents can be prepared by the attachment of magnetic iron oxides nano- or microparticles on the surface or within the pores of the treated materials. Magnetic materials can be easily separated from complex systems and difficult-to-handle media by means of magnetic separators (Safarikova & Safarik, 2001).

In order to improve manipulation with *Posidonia* biomass, magnetically responsive derivatives were prepared using three simple and low-cost procedures and tested as magnetic biosorbents for organic dyes removal. The best magnetic *Posidonia* adsorbent was characterized in detail.

Materials and Methods

Materials

Posidonia oceanica fibres balls, collected at the Poetto beach in Cagliari (Sardinia, Italy; the coordinates of the area are 39°11'43.50" N – 9°09'33.52" E) at the end of March 2013, were manually converted into fibres, washed thoroughly with water to remove sand and salt and then dried in an oven at 40 - 60 °C for 48 h to a constant weight. After drying, the fibres were cut into small fragments and milled to obtain fine particles (length ca 0.1 – 0.6 mm, width ca 0.03 – 0.1 mm), see Fig. 2. Methylene blue (C.I. 52015), Bismarck brown Y (C.I. 21000) and safranin O (C.I. 50240) were purchased from Sigma, USA. Crystal

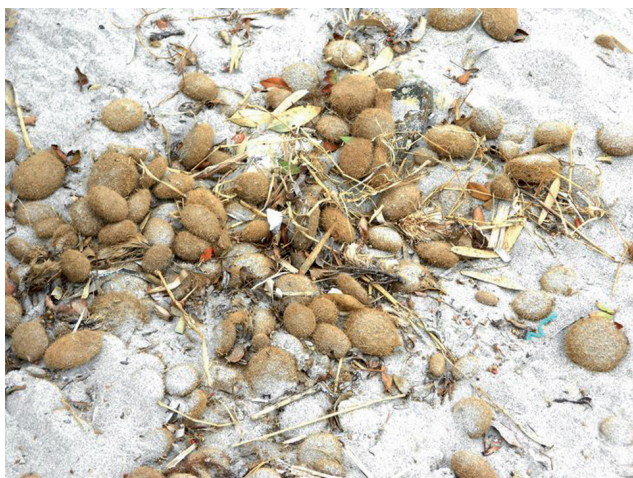


Fig. 1: “Neptune balls” (*Posidonia oceanica* dead biomass) on the Poetto beach, Cagliari, Sardinia, Italy.

violet (C.I. 42555) and brilliant green (C.I. 42040) were supplied by Lachema, Czech Republic. Acridine orange (C.I. 46005) was obtained from Loba Feinchemie, Austria, while Nile blue A sulphate (C.I. 51180) was from Chemische Fabrik GmbH, Germany. Common chemicals were from Sigma-Aldrich, Czech Republic. Water-based ionic magnetic fluid stabilized with perchloric acid (concentration 30.5 mg of maghemite per 1 mL) was prepared using a standard procedure (Massart, 1981).

Magnetic modification of *Posidonia* powdered biomass

a/ Microwave assisted modification procedure

Posidonia biomass was magnetically modified using microwave-synthesized magnetic iron oxides particles (Safarik & Safarikova, 2014). In a typical procedure, 1 g $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ was dissolved in 100 mL of water in a 600 – 800 mL beaker and solution of sodium or potassium hydroxide (1 mol L^{-1}) was added slowly under mixing until the pH reached the value ca 12; during this process, a precipitate of iron hydroxides was formed. The suspension was then diluted up to 200 mL with water and inserted into a standard kitchen microwave oven (700 W, 2450



Fig. 2: *Posidonia oceanica* fibres ball, separated fibres and fine biomass particles obtained by milling.

MHz). The suspension was usually treated for 10 min at the maximum power. Then the beaker was removed from the oven and the formed magnetic iron oxides nano- and microparticles were repeatedly washed with water until neutral pH of the magnetic suspension was reached.

To prepare magnetically responsive *Posidonia* biomass, one gram of biomass was thoroughly mixed in a short test-tube or a small beaker with 2 mL of microwave iron oxides nano- and microparticles suspension (1 part of completely sedimented iron oxides particles and 4 parts of water). Vigorous mixing with a spatula or laboratory spoon enabled homogeneous distribution of magnetic nano- and microparticles within the treated material. This mixture was allowed to dry completely at temperatures not exceeding 60 °C for 48 hours. In order to increase magnetic response of the *Posidonia* composite, the amount of iron oxide particles can be increased (Safarik & Safarikova, 2014).

b/ Mechanochemical modification procedure

In the standard procedure, a mixture of 1.35 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.005 mol), 0.50 g of $\text{FeCl}_2 \cdot 4 \text{H}_2\text{O}$ (0.0025 mol) and 4 g of sodium chloride (inert material used to avoid particles agglomeration) was ground in a mortar at room temperature for 10 min. One g of *Posidonia* biomass was then added and after thorough mixing, the process continued for another 10 min. As the last step, powdered potassium hydroxide (1.22 g) was added and after mixing, the grinding continued for 10 min. After KOH addition, the mixture became brown. During the grinding process, the material was scraped from the mortar wall occasionally. After finishing the mechanochemical process, the magnetically modified material was thoroughly washed with water (to remove soluble impurities and free iron oxides particles) and air dried (Safarik *et al.*, 2014).

c/ Modification with magnetic fluid

In a typical procedure, 1 g of *Posidonia* biomass was thoroughly mixed in a short test-tube or a small beaker with 1 mL of water based ferrofluid stabilized with perchloric acid. The mixing with a spatula or laboratory spoon enabled homogeneous distribution of magnetic fluid within the treated biomass. This mixture was allowed to dry completely at temperatures not exceeding 50 °C and then washed with water and/or methanol. The magnetically responsive biomass was air dried (Safarik *et al.*, 2012a).

Adsorption of dyes on magnetic *Posidonia* biomass

The following procedure was employed to study the adsorption properties (Safarik *et al.*, 2012b). 30 mg of magnetically modified *Posidonia* biomass were mixed with 4.0 mL of water in a test tube. Then 1-6 mL portion of stock water solution (1 mg mL^{-1}) of a tested dye was added and the total volume of the solution was made up to 10.0 mL with water. The suspension was mixed for 2

h at room temperature. Then the magnetic adsorbent was separated from the suspension by means of a magnetic separator (MPC-1 or MPC-6, Dynal, Norway) and the clear supernatant was used for the spectrophotometric measurement. The concentration of free (unbound) dye in the supernatant (C_{eq}) was determined from the calibration curve. The amount of dye bound to the unit mass of the adsorbent (q_{eq}) was calculated using the following formula:

$$q_{eq} = V(C_0 - C_{eq}) / m \quad (1)$$

where V is the total volume (L), C_0 is the initial concentration (mg L^{-1}) of dye used in the experiment and m is the mass of adsorbent (g). The value q_{eq} was expressed in mg of adsorbed dye per 1 g of adsorbent. Equilibrium adsorption data were fitted to Langmuir adsorption isotherms using SigmaPlot software.

Adsorption kinetics

Adsorption kinetics was studied using Bismarck brown Y (initial dye concentration 150 mg L^{-1} , 25°C , pH not adjusted), in different time intervals (0-300 min). The amount of adsorbed dye per unit mass of adsorbent q_t (mg g^{-1}) in time t was calculated from this formula:

$$q_t = V(C_0 - C_t) / m \quad (2)$$

where C_t is the concentration of dye in solution (mg L^{-1}) in time t (min). The obtained kinetic data were analyzed using the linear forms of pseudo-first (Lagergren, 1898) and pseudo-second (Kumar, 2006) order kinetic equations given as follows, respectively:

$$\ln(q_{eq} - q_t) = \ln(q_{eq}) - k_1 t \quad (3)$$

where the rate constant k_1 (min^{-1}) can be obtained from the linear plot of $\ln(q_{eq} - q_t)$ against time

$$t/q_t = 1/k_2 q_{eq}^2 + t/q_{eq} \quad (4)$$

where the equilibrium adsorption capacity (q_{eq}) and the second-order rate constant k_2 ($\text{g mg}^{-1} \text{ min}^{-1}$) can be determined from the slope and intercept of plot t/q_t versus t .

Thermodynamic studies

The studies of temperature effect of Bismarck brown Y adsorption on magnetically modified *Posidonia* biomass were carried out at 282.15, 298.15 and 313.15 K.

The thermodynamic equilibrium constant K_d was determined from intercept of the plot of $\ln(q_{eq}/C_{eq})$ against q_{eq} (Khan & Singh, 1987). The other thermodynamic pa-

rameters, namely Gibbs free energy change ΔG° (J mol^{-1}), standard enthalpy change ΔH° (J mol^{-1}) and standard entropy change ΔS° ($\text{J mol}^{-1} \text{ K}^{-1}$) of studied process were calculated by using these equations:

$$\Delta G^\circ = -RT \ln(K_d) \quad (5)$$

$$\ln(K_d) = \Delta S^\circ/R - \Delta H^\circ/RT \quad (6)$$

where R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the absolute temperature (K). ΔH° and ΔS° were determined from the slope and intercept of the linear plot of $\ln(K_d)$ versus $1/T$.

Results and Discussion

Magnetic modification of *Posidonia* biomass

Three procedures for magnetic modification of *Posidonia* biomass, namely modification with microwave synthesized magnetic iron oxides nano- and microparticles (Safarik & Safarikova, 2014), mechanochemical synthesis (Safarik *et al.*, 2014) and modification with water based magnetic fluid (Safarik *et al.*, 2012a) were tested in order to select an optimal magnetized adsorbent. Both the adsorbent maximum adsorption capacity and the simplicity and price of its preparation were taken into account. Preliminary adsorption experiments with methylene blue showed that magnetization with microwave synthesized magnetic iron oxides nano- and microparticles enabled to prepare magnetic adsorbent with the highest maximum adsorption capacity (calculated using Langmuir adsorption isotherm), see Table 1. This magnetization procedure is extremely simple, and very cheap chemicals (ferrous sulphate and sodium or potassium hydroxide) are used as precursors. During the microwave-assisted synthesis, magnetic iron oxide nanoparticles (ca 25 to 100 nm) formed micrometer-sized stable aggregates (maximum aggregate size ca 20 μm ; Baldikova *et al.*, in press). Magnetic modification led to the deposition of iron oxide nanoparticle aggregates on the surface of the *Posidonia* biomass providing sufficient surface area for efficient dye adsorption (see Fig. 3). Energy-dispersive X-ray spectroscopy confirmed the presence of iron on the magnetized biomass (Fig. 4). The presence of Fe^{3+} ions on the surface of magnetically modified *Posidonia* biomass was confirmed by Perls' Prussian Blue Stain that caused intensive blue coloration of the whole material (Fig. 5). The stability of magnetically modified biomass was very high (stable at least two months in water suspension). The formed magnetically responsive *Posidonia*

Table 1. Maximum adsorption capacity (q_{max}) of magnetic *Posidonia* adsorbents for methylene blue.

Magnetic modification of <i>Posidonia</i> adsorbents	q_{max} (mg g^{-1})
Microwave synthesized magnetic iron oxides nano- and microparticles	143.7
Mechanochemical synthesis	102.5
Modification with magnetic fluid	133.3

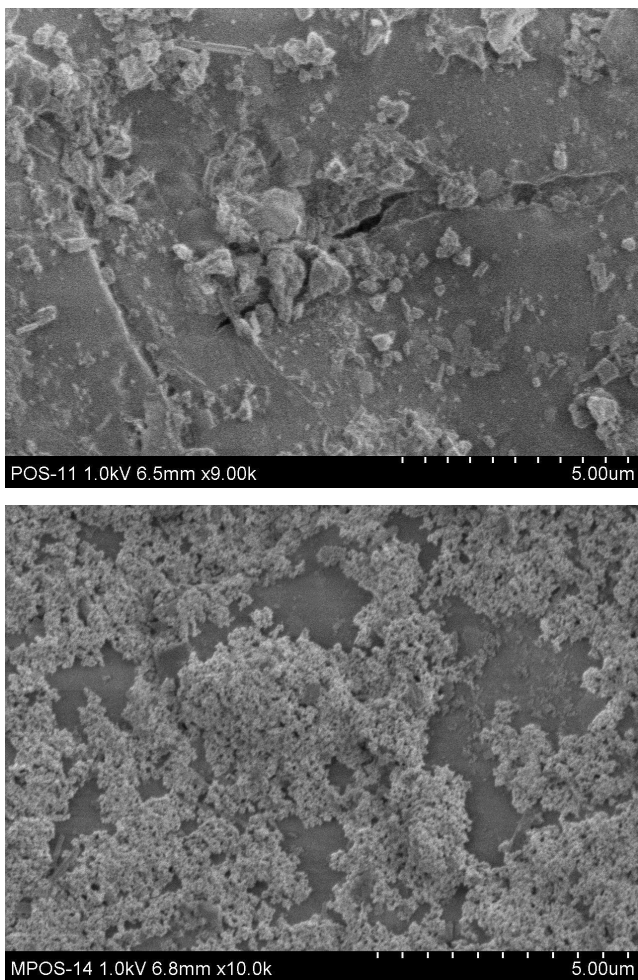


Fig. 3: SEM images of native (top) and magnetically modified (bottom) *Posidonia* biomass.

adsorbent can be easily separated using permanent magnet or commercial magnetic separator (Fig. 6).

Adsorption studies and isotherms

Posidonia biomass modified with microwave synthesized magnetic iron oxides nano- and microparticles was used as an adsorbent to study binding of 7 organic water-soluble dyes belonging to different dye classes. These dyes were selected according to the results of the preliminary screening experiment using 18 different dyes.

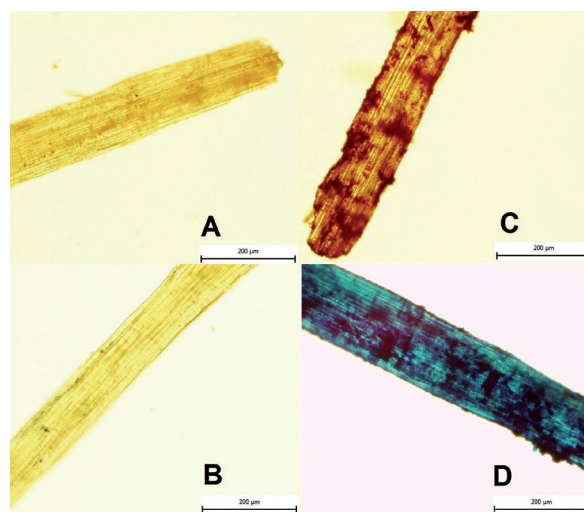


Fig. 5: Optical microscopy of native (A) and magnetically modified (C) *Posidonia* biomass. After Perls' stain, almost no coloration is visible on native biomass (B), while deep blue coloration is observed on magnetically modified biomass (D). Bar is 200 μm.

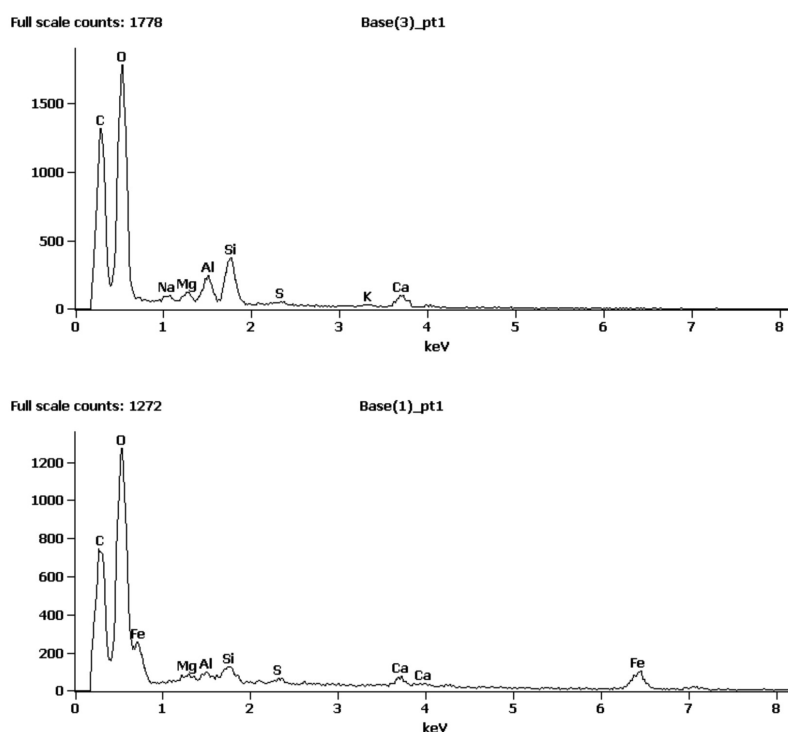


Fig. 4: EDS of native (top) and magnetically modified (bottom) *Posidonia* biomass.



Fig. 6: Appearance of original *Posidonia* biomass suspension (left), suspension of biomass after magnetic modification (middle) and demonstration of magnetic separation of magnetically modified biomass (right).

Therefore, Bismarck brown Y (azodyes group), crystal violet and brilliant green (triphenylmethane group), methylene blue (quinone-imine group), acridine orange (acridine group), Nile blue (oxazin group) and safranin O (safranin group) were chosen for further experiments. The chemical structures are shown in Table 2.

The contact time is one of the most important adsorption parameters required for determination of time necessary to reach the equilibrium. As can be seen from the Fig. 7, the adsorption process was very fast; more than 96% of Bismarck brown Y was adsorbed within 5 min. However, to reach the equilibrium approximately 1 h is needed. Two hours incubation was used for the adsorption experiments. The equilibrium adsorption isotherms

Table 2. Dye structures and maximum adsorption capacities (q_{max}) and dissociation constants (b) describing the dyes adsorption on magnetically modified *Posidonia* biomass, calculated from the Langmuir equation; q_{max} is expressed in mg g^{-1} .

Dye	Dye structure	Adsorption coefficients
Acridine orange	 $\cdot \frac{1}{2}\text{ZnCl}_2$ $\cdot \text{HCl}$	$q_{max} = 119.8$ $b = 0.424$
Bismarck brown Y	 $\cdot 2\text{HCl}$	$q_{max} = 233.5$ $b = 0.084$
Brilliant green	 $\text{HO}-\text{S}(=\text{O})_2-\text{O}^-$	$q_{max} = 151.8$ $b = 0.588$
Crystal violet	 Cl^-	$q_{max} = 99.9$ $b = 0.299$
Methylene blue	 Cl^- $\cdot x\text{H}_2\text{O}$	$q_{max} = 143.7$ $b = 0.060$
Nile blue A sulphate	 $\text{O}=\text{S}(=\text{O})_2-\text{O}^-$	$q_{max} = 193.7$ $b = 0.041$
Safranin O	 Cl^-	$q_{max} = 88.1$ $b = 0.307$

for the tested dyes using magnetically modified *Posidonia* biomass are shown in Fig. 8.

In order to study the adsorption process, Langmuir and Freundlich isotherm equations are usually used for experimental data analysis. The Langmuir model is valid for monolayer adsorption onto a surface with a finite number of identical sites. The well-known expression for the Langmuir model is given by

$$q_{eq} = \frac{q_{max} b C_{eq}}{1 + b C_{eq}} \quad (7)$$

where q_{eq} (expressed in mg g^{-1} or mg mL^{-1}) is the amount of the adsorbed dye per unit mass or sedimented volume of magnetic *Posidonia* biomass and C_{eq} (expressed in mg L^{-1}) is the unadsorbed dye concentration in solution at equilibrium. The parameter q_{max} is the maximum amount of the dye per unit mass (mg g^{-1}) or sedimented volume (mg mL^{-1}) of magnetic *Posidonia* biomass to form a complete monolayer on the surface bound at high dye concentration and b is a constant related to the affinity of the binding sites (expressed in L mg^{-1}) (Safarik *et al.*, 2012b).

Non-linear regression calculation using SigmaPlot software was used to fit the experimental data to Langmuir adsorption model and to obtain both constants (q_{max} , b). The results are presented in Table 2. The value of the maximum adsorption capacity is a very important parameter describing the adsorption process.

In the case of seven tested dyes, the highest calculated q_{max} was found for Bismarck brown Y (233.5 mg g^{-1}), while the lowest q_{max} value was obtained for safranin O (88.1 mg g^{-1}).

Adsorption kinetics

As already shown in the Fig. 7, the adsorption process was very fast with more than 96% of Bismarck brown Y adsorbed within 5 min. The obtained data were subsequently analyzed to investigate kinetics of adsorption process using pseudo-first and pseudo-second order kinetic models. It is apparent from results summarized in Table 3 that the pseudo-first order kinetic model did not fit well; the correlation coefficient was low and the calculated q_{eq} absolutely disagreed with the experimental $q_{eq\text{exp}}$ value, while in case of pseudo-second order kinetic model (see Table 3 and Fig. 9) the correlation coefficient reached the value close to 1.0 and the theoretical q_{eq} value calculated from this equation approached the experimental $q_{eq\text{exp}}$.

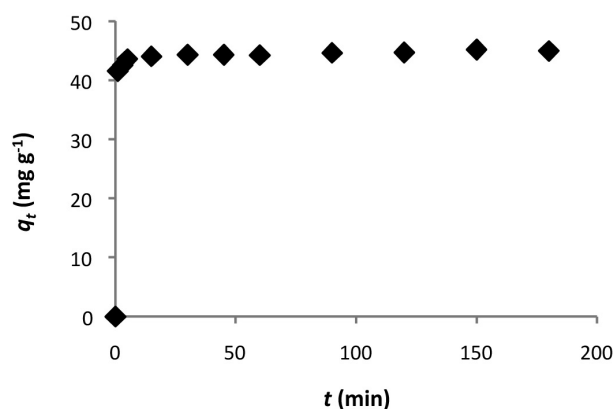


Fig. 7: Dependence of Bismarck brown Y adsorption on time (dye initial concentration 150 mg L^{-1} , 25°C , pH not adjusted).

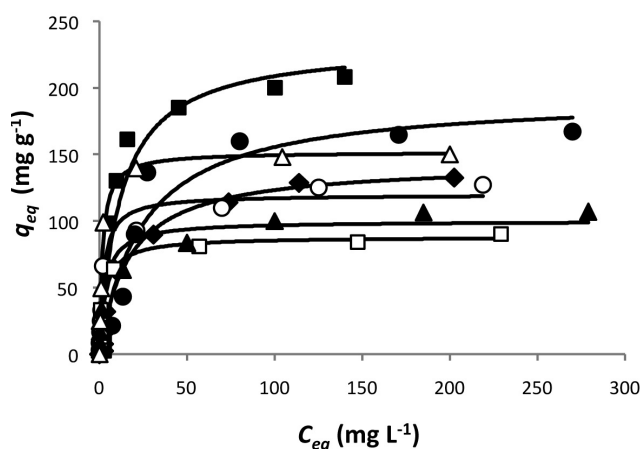


Fig. 8: Equilibrium adsorption isotherms of tested dyes on magnetically modified *Posidonia* biomass. C_{eq} - equilibrium liquid-phase concentration of the unadsorbed (free) dye (mg L^{-1}); q_{eq} - equilibrium solid-phase concentration of the adsorbed dye (mg g^{-1}). (\circ) - acridine orange; (\blacksquare) - Bismarck brown Y; (\triangle) - brilliant green; (\blacktriangle) - crystal violet; (\blacklozenge) - methylene blue; (\bullet) - Nile blue; (\square) - safranin O.

Thermodynamic studies

Thermodynamic studies were performed at three different temperatures, namely 282.15, 298.15 and 313.15 K. All obtained thermodynamic parameters are presented in Table 4. Negative values of Gibbs free energy change (ΔG°) indicate the spontaneous process, positive ΔH° the endothermic nature of adsorption and positive ΔS° suggests an increase of the randomness at the solid/solution

Table 3. The pseudo-first and pseudo-second order kinetic model parameters for Bismarck brown Y (25°C , pH not adjusted).

C_o (mg L^{-1})	$q_{eq\text{exp}}$ (mg g^{-1})	Pseudo-first order			Pseudo-second order		
		k_1 (min^{-1})	q_{eq} (mg g^{-1})	R^2	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	q_{eq} (mg g^{-1})	R^2
150	45.2	0.0137	2.0	0.7593	0.0632	45.0	0.9999

Table 4. The thermodynamic parameters for Bismarck brown Y adsorption on magnetically modified *Posidonia oceanica*.

ΔH° (kJ mol ⁻¹)	ΔS° (kJ mol ⁻¹ K ⁻¹)	ΔG° (kJ mol ⁻¹)		
		282.15	298.15	313.15
14.977	0.073	-5.514	-7.235	-7.731

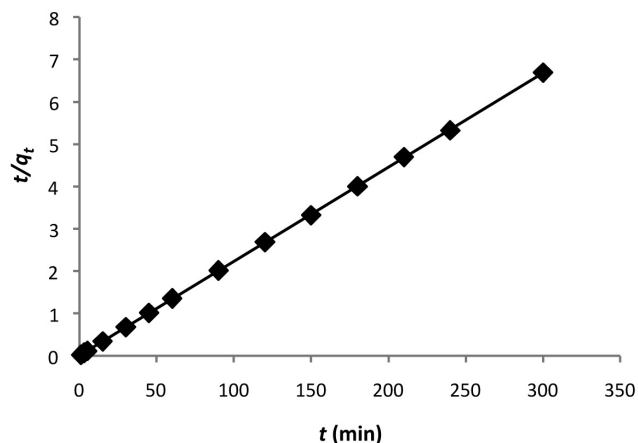


Fig. 9: The pseudo-second order kinetic model plot (Bismarck brown Y, initial concentration 150 mg L⁻¹, pH not adjusted, 25°C).

interface during sorption process. Similar results have been published recently (Cengiz & Cavas, 2010).

Conclusions

Posidonia oceanica dead biomass, known also as Neptune balls, was chosen to study the biosorption of selected organic water-soluble dyes. This material can be obtained at very low cost; in fact in many localities it is a waste. To simplify the manipulation with the adsorbent, *Posidonia* biomass was magnetically modified using three different techniques. Although all tested magnetization procedures led to the preparation of magnetically responsive adsorbents, the method using microwave synthesized magnetic iron oxides nano- and microparticles enabled to prepare material with the highest dye removal efficiency.

Langmuir adsorption model, enabling very simple calculation of maximum adsorption capacities, could be applied with reasonable accuracy for fitting all the experimental adsorption data. The obtained values of maximum adsorption capacity ranged between 88.1 mg g⁻¹ for saffranin O and 233.5 mg g⁻¹ for Bismarck brown Y, respectively.

The adsorption processes could be described by the pseudo-second-order kinetic model and the thermodynamic studies indicated that the adsorption is spontaneous and endothermic. Due to the low price, high adsorption efficiency and simplicity of magnetic modification process, the magnetic *Posidonia* biomass represents a perspective low-cost adsorbent for organic pollutants removal.

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