



Organic dyes removal using magnetically modified rye straw



Eva Baldikova^{a,*}, Mirka Safarikova^a, Ivo Safarik^{a,b,**}

^a Department of Nanobiotechnology, Institute of Nanobiology and Structural Biology of GCRC, Na Sadkach 7, 370 05 Ceske Budejovice, Czech Republic

^b Regional Centre of Advanced Technologies and Materials, Palacky University, Slechtitelu 11, 783 71 Olomouc, Czech Republic

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ABSTRACT

Rye straw, a very low-cost material, was employed as a biosorbent for two organic water-soluble dyes belonging to different dye classes, namely acridine orange (acridine group) and methyl green (triarylmethane group). The adsorption properties were tested for native and citric acid–NaOH modified rye straw, both in nonmagnetic and magnetic versions. The adsorption equilibrium was reached in 2 h and the adsorption isotherms data were analyzed using the Langmuir model. The highest values of maximum adsorption capacities were 208.3 mg/g for acridine orange and 384.6 mg/g for methyl green.

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1. Introduction

Enormous amounts of dyestuff are consumed annually by various sectors of industry, e. g. textile, paper, leather, plastics, rubber, cosmetics, pharmaceuticals and food industries [1]. These compounds or their metabolites cause concern for human health because of their toxicity, carcinogenicity and mutagenity [2,3] and also due to high persistence in environment and non-biodegradable characteristics [4]. Moreover, the colored dye effluents can block the penetration of sunlight and oxygen which are both essential for various aquatic forms of life [5].

Many techniques have been employed to eliminate dyes from waste water. These methods involve e.g. ion exchange, coagulation and flocculation, oxidation and various forms of degradation (photo-, bio- and chemical-) [4,6]. Among them, adsorption is considered to be superior because of the high efficiency and subsequently economical value [7].

In recent years, many plant materials have been tested as low-cost adsorbents for various xenobiotics, such as organic dyes, heavy metals, radionuclides or endocrine disruptors. For instance, wheat straw [8], barley straw [9], rice straw [10], rice husks [11], sawdust [1], tea waste [5], peanut husks [12], spent coffee grounds [13],

coffee husks [14], spent grain [15], fruit peels [16] and sugarcane bagasse [17] have been successfully used for organic dyes removal.

Rye straw represents a very interesting material that can be obtained in large amount and for low price. Nevertheless, there are only few publications focused on utilization of rye derivatives for xenobiotics removal. One of them describes adsorption of Cr (VI) [18] and the second one removal of azodyes [19].

Native plant materials usually show lower maximum adsorption capacities. Nevertheless, these values can be significantly increased using a suitable method such as treatment with various acids, hydroxides or combination of both; also less common carbonization or hydrolysis have been reported recently [9,11].

A successful combination of nonmagnetic powdered material with magnetic nano- or microparticles (often bound on the surface or within the pores of the modified material) results in a formation of magnetically responsive (bio)composites which exhibit response to external magnetic field. Magnetic materials facilitate and accelerate many manipulations, also in difficult-to-handle materials (including raw extracts, blood and other body fluid, environmental samples, cultivation media, suspensions, etc.) [20]. Originally diamagnetic materials can be easily and selectively separated using a permanent magnet, an appropriate magnetic separator or an electromagnet. Magnetic separations can also be performed in large scale due to the existence of industrial magnetic separators, currently employed e.g. in kaolin decolorization, steel industry, mineral beneficiation, etc. [20].

The aim of this paper is the comparison of adsorption properties of native and chemically modified rye straw, both in nonmagnetic and magnetic versions for organic dyes adsorption and a demonstration of the promising potential of this type of plant-based material.

* Corresponding author.

** Corresponding author at: Department of Nanobiotechnology, Institute of Nanobiology and Structural Biology of GCRC, Na Sadkach 7, 370 05 Ceske Budejovice, Czech Republic.

E-mail addresses: baldie@email.cz (E. Baldikova), ivosaf@yahoo.com (I. Safarik).

2. Materials and methods

2.1. Materials

Rye straw was supplied by the farm Tomsik in Horni Dubenky (Czech Republic). Ferrous sulfate heptahydrate and sodium hydroxide were from Sigma-Aldrich (Czech Republic), citric acid from Lachema (Czech Republic), acridine orange (CI (Colour Index) 46005) and methyl green (CI 42585) from Loba Feinchemie (Austria).

2.2. Preparation of rye derivative

Before all experiments, rye straw was cut into smaller pieces (ca. 5 cm), milled and sieved to obtain fine particles about 0.1–2 mm in diameter.

2.3. Magnetic modification

Magnetic modification was carried out according to the described procedure [21] using microwave-synthesized magnetic iron oxide nano- and microparticles. Briefly, 1 g $\text{Fe}(\text{SO}_4) \cdot 7\text{H}_2\text{O}$ was dissolved in 100 mL of water and solution of NaOH (mol/L) was added dropwise under stirring until the pH reached the value 12

and the precipitate of iron hydroxides was formed. Then the suspension was diluted up to 200 mL with water. The beaker was inserted into a standard kitchen microwave oven (700 W, 2450 MHz) and treated at maximum power for 10 min. Finally, the formed magnetic particles were repeatedly washed with water until the pH was neutral.

To prepare magnetic biosorbent derivate, 1 g of straw was thoroughly mixed with 2 mL of magnetic iron oxide nano- and microparticles suspension (1 part of completely sedimented magnetic particles and 4 part of water) and then this mixture was dried at 60 °C for 24 h.

2.4. Citric acid–NaOH modification

The chemical modification of rye straw was performed as described previously [2]. Citric acid (0.5 mol/L) was added to rye straw in a ratio 12:1 (v/w). This mixture was stirred for 30 minutes and dried at 50 °C for 24 h. The thermochemical reaction between rye straw and citric acid (CA) was carried out by increasing the temperature to 120 °C for 60 min. After cooling at room temperature, the CA-modified straw was thoroughly washed with distilled water to obtain neutral pH and filtered. Then a solution of NaOH (0.1 mol/L) was added to the filtrated residues in a ratio 12:1 (v/w) and the mixture was stirred for 90 min. Finally, the CA–NaOH modified straw derivative was extensively washed with distilled water to remove alkali residuals and dried at 50 °C for 24 h.

2.5. Adsorption of dyes on rye straw biomass

Testing of the adsorption properties slightly differed for untreated and chemically modified dye straw. In case of untreated derivative, 30 mg of biosorbent was mixed with 1 mL of distilled water and then 1–9 mL of dye (mg/mL) was added, while in the

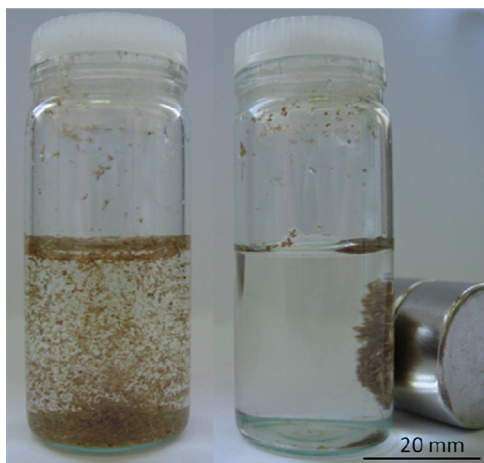


Fig. 1. Magnetic separation of magnetically modified rye straw using NdFeB permanent magnet (diameter: 20 mm; height: 10 mm; remanence: 1 T).

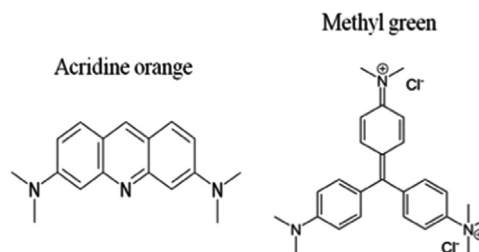


Fig. 3. Chemical structures of acridine orange and methyl green.

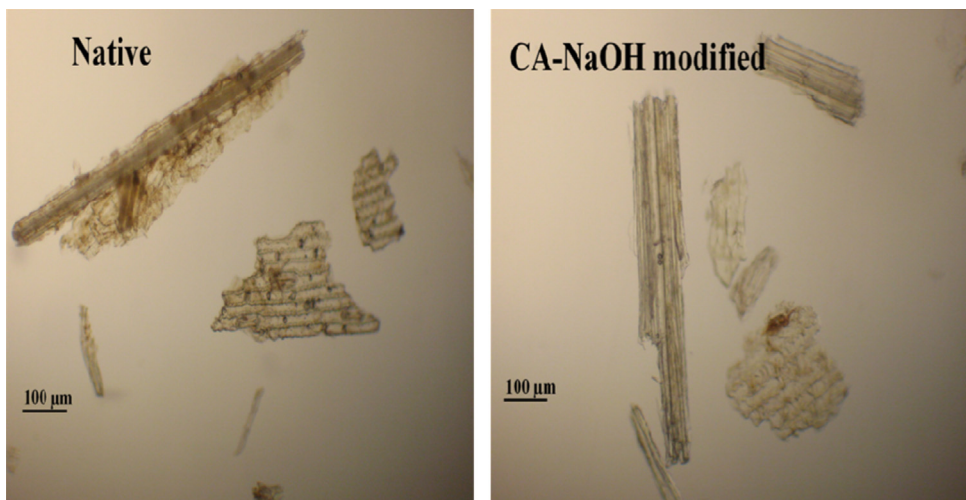


Fig. 2. Structures of native (left) and chemically modified (right) rye straw adsorbents.

Table 1

Other adsorbents for acridine orange and methyl blue removal. The maximum adsorption capacities (Q_{\max}) were calculated using the Langmuir or Langmuir–Freundlich models.

Dye	Adsorbent	Q_{\max} (mg/g)	Other notes	Reference
Acridine orange	Calcium alginate beads	41.8	Optimal pH 5–8	[22]
	Graphene alginic beads	61.3		
	Graphene oxide/calcium alginate beads	59.0		
	Graphene oxide/alginic beads	63.3		[23]
	ZSM-5 nanozeolit	55.5	Optimal pH 9–11	
	Fe-ZSM-5 nanozeolit	64.9	Q_{\max} increases with increasing temperature	
	Spent coffee grounds/magnetic fluid	73.4	Used also for magnetic solid phase extraction	[13]
	Peanut husks/magnetic fluid	71.4	Equilibrium 60–90 min	[12]
	Magnetic particles (γ - Fe_2O_3)	59.0	Optimal pH 4–8	[24]
	<i>Kluyveromyces fragilis</i> /magnetic fluid	59.1	Equilibrium 60–90 min	[25]
	Spruce sawdust/magnetic fluid	24.1	Served also as an absorbent for lysozyme	[26]
	Native rye straw	42.9	Equilibrium in 2 h	This work
	Rye straw/microwave-synthesized magnetic iron oxides	36.9		
	Citric acid–NaOH rye straw	192.3		
	Citric acid–NaOH rye straw/ microwave-synthesized magnetic iron oxides	208.3		
Methyl green	Graphene sheets	203.5–312.8	Q_{\max} increases with increasing temperature	[27]
	Graphene sheets decorated with CoFe_2O_4	147.1–149.8		
	Native rye straw	95.2	Equilibrium in 2 h	This work
	Rye straw/microwave-synthesized magnetic iron oxides	78.1		
	Citric acid–NaOH rye straw	384.6		
	Citric acid–NaOH rye straw/ microwave-synthesized magnetic iron oxides	357.1		

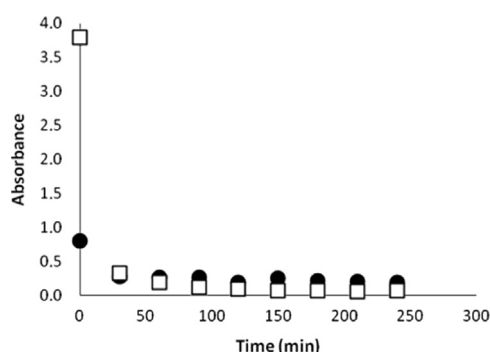


Fig. 4. Time necessary to reach the adsorption equilibrium for methyl green (● native and □ chemically modified).

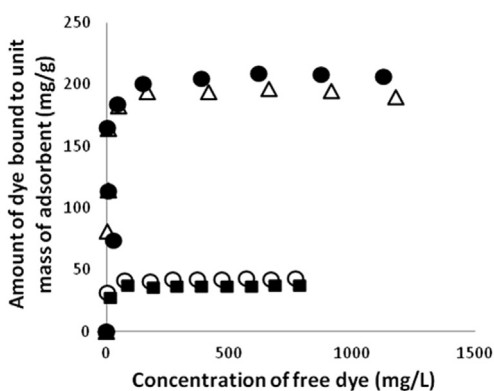


Fig. 5. The Langmuir isotherms for differently modified rye straw (○ native nonmagnetic, ■ native magnetic, △ CA–NaOH modified, ● magnetic CA–NaOH) and acridine orange.

second case, 30 mg of CA–NaOH straw was mixed with 4 mL of distilled water and 1–6 mL of dye (5 mg/mL) was added. The final volume was made up to 10 mL with distilled water. Both types of adsorbents were incubated for 3 h at room temperature.

Subsequently the nonmagnetic derivatives were centrifuged out (8 min at 10000 g), while the magnetic materials were separated by means of magnetic separator (DynaMag™-15, Dynal,

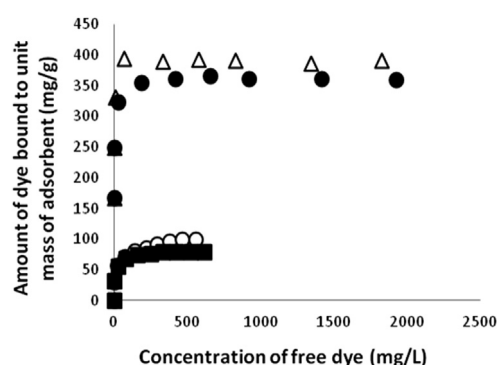


Fig. 6. The Langmuir isotherms for differently modified rye straw (○ native nonmagnetic, ■ native magnetic, △ CA–NaOH modified, ● magnetic CA–NaOH) and methyl green.

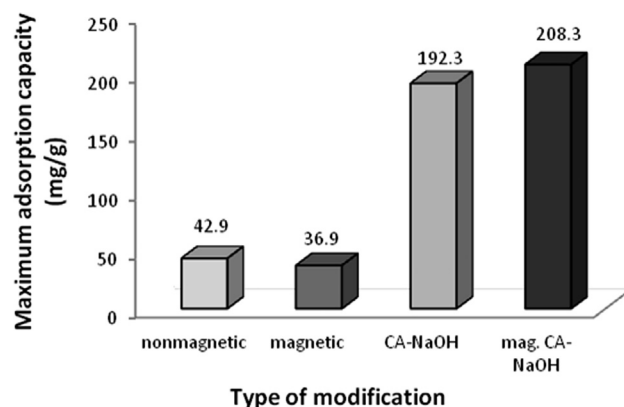


Fig. 7. Comparison of the maximum adsorption capacities for differently modified rye straw and acridine orange.

Norway) and the clear supernatant was used for spectrophotometric measurement (UV/VIS Spectrophotometer Cintra 20, GBC, Australia). 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})

Table 2
Some published methods for increasing of Q_{\max} of straw.

Type of straw	Modification	Removal of	Other notes	References
Wheat	Graft copolymerization	Ammonium; phosphate	Potassium acrylate/polyvinylalcohol	[28]
	Succinoylation	Cr (VI)	Succinic anhydride, dimethylacetamide, catalyst 4-dimethylaminopyridine	[29]
	Esterification	Methyl orange; Acid green 25	30% NaOH, trimethylammonium chloride	[30]
	Mild acid hydrolysis	Methylene blue; Red Basic 22	100 °C, 18 M H ₂ SO ₄ ; Q_{\max} increased 3 times (RB22) and 9 times (MB)	[31]
	Surfactant modification	Acid blue 40; reactive black 5	Cetylpyridinium chloride	[32]
	Grafting method and amine-cross-linking	NO ₃ ⁻ , PO ₄ ³⁻ , Cr ₂ O ₇ ²⁻	Epichlorohydrin, triethylamine and ethylenediamine	[33]
		Acid Red 73; Reactive Red 24		[4]
	Solid-phase esterification	Copper ion; methylene blue	Citric acid–NaOH treatment with addition of Pb(NO ₃) ₂ , Q_{\max} increased ca 6 times	[34]
		Copper ion	Citric acid–NaOH treatment, 11 times higher Q_{\max}	[8]
	Alkalization	Cu (II)	Treatment with 5% NaOH, 1% NaOH and 5% NaOH in combination with formaldehyde	[35]
Rice	Carbonization	Cr (III)	2N NaOH, stirred for 10 min, left overnight	[36]
		Cr (VI)	No activation process	[37]
	Alkalization with cross-linking	U (VI)	25% NaOH+epichlorohydrin	[38]
	Mercapto-grafting	Hg (II)	1.5% 3-Mercaptopropyltriethoxysilane	[39]
	Acetylation	Oil spill	Acetic anhydride, 100 and 120 °C, 1–4 h, 4 tertiary amine catalysts	[40]

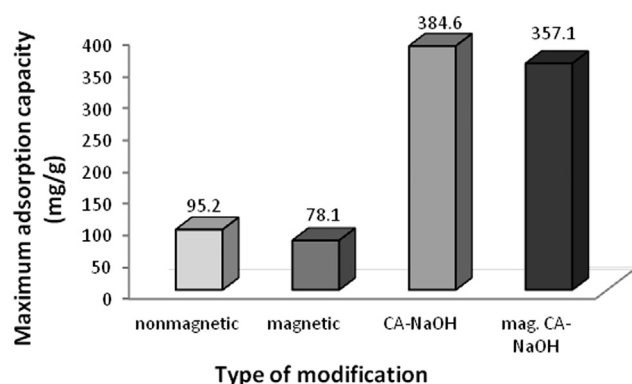


Fig. 8. Comparison of the maximum adsorption capacities for differently modified rye straw and methyl green.

was calculated using the following formula:

$$Q_{\text{eq}} = (0.01C_{\text{tot}} - 0.01C_{\text{eq}}) / 0.03 \quad (\text{mg/g})$$

where C_{tot} is the total (initial) concentration ($\mu\text{g/mL}$) of dye used in the experiment.

3. Results and discussion

As can be seen on Fig. 1, magnetic modification of rye straw by microwave synthesized magnetic iron nano- and microparticles led to a formation of magnetically responsive material reacting to external magnetic field. During this procedure the whole amount of straw was magnetically modified. The presence of magnetic particles on the surface was detected using Perl's Prussian Blue Stain causing intense blue color of the Fe³⁺ containing material.

It was proven that the stability of magnetically modified straw is very high. This material can be stored in water suspension (at 4 °C) more than six months without releasing magnetic particles or other negative changes.

No substantial morphological differences in the structure of native and chemically modified rye straw were found as demonstrated in Fig. 2.

Rye straw derivatives were tested as potential adsorbents for two types of organic water-soluble dyes, namely acridine orange belonging to acridine group and methyl green representing triarylmethane group. Their chemical structures are illustrated in Fig. 3. Table 1 shows some published adsorption data of various adsorbent which have been recently used for acridine orange and methyl green removal.

The time necessary to reach the adsorption equilibrium was equal to approximately two hours for both native and chemically modified rye straw as shown in Fig. 4. Nevertheless, the incubation of all experiments was performed for three hours.

The adsorption properties of the prepared adsorbents were analyzed using the Langmuir isotherms (Figs. 5 and 6) and the maximum adsorption capacities (Q_{\max}) were calculated by linear regression of these isotherms. The comparison of Q_{\max} values is demonstrated in Fig. 7 (for acridine orange) and Fig. 8 (for methyl green). As can be seen from these figures, the presence of magnetic particles in native versions of straw slightly decreased the maximum adsorption capacities. After chemical modification, some significant differences in adsorption properties of tested dyes appeared. In the case of acridine orange, the magnetic Ca–NaOH rye straw derivatives reached higher maximum adsorption capacities than the nonmagnetic derivatives, while the trend for methyl green is opposite.

It is apparent that citric acid–NaOH modification considerably increased the maximum adsorption capacities, in all cases more than four times. Many published studies have been focused on improvement of adsorption properties of various types of straw recently. Some of these methods can be seen in Table 2.

4. Conclusion

The results clearly demonstrate that rye straw derivatives, especially the one obtained by after citric acid–NaOH modification, can be considered as a very promising low-cost material for various types of organic dyes removal. The manipulation with adsorbents can be significantly facilitated after their conversion into magnetically responsive materials using microwave-synthesized magnetic nano- or microparticles.

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References

- [1] S. Hashemian, M. Salimi, Nano composite a potential low cost adsorbent for removal of cyanine acid, *Chem. Eng. J.* 188 (2012) 57–63.
- [2] R. Gong, Y. Jin, F. Chen, J. Chen, Z. Liu, Enhanced malachite green removal from aqueous solution by citric acid modified rice straw, *J. Hazard. Mater.* 137 (2006) 865–870.
- [3] S. Chakraborty, S. Chowdhury, P. Das Saha, Artificial neural network (ANN) modeling of dynamic adsorption of crystal violet from aqueous solution using citric-acid-modified rice (*Oryza sativa*) straw as adsorbent, *Clean Technol. Environ. Policy* 15 (2013) 255–264.
- [4] X. Xu, B.-Y. Gao, Q.-Y. Yue, Q.-Q. Zhong, Preparation and utilization of wheat straw bearing amine groups for the sorption of acid and reactive dyes from aqueous solutions, *J. Hazard. Mater.* 182 (2010) 1–9.
- [5] T. Madrakian, A. Afkhami, M. Ahmadi, Adsorption and kinetic studies of seven different organic dyes onto magnetite nanoparticles loaded tea waste and removal of them from wastewater samples, *Spectrochim. Acta Part A-Mol. Biomol. Spectrosc.* 99 (2012) 102–109.
- [6] W. Zhang, H. Yan, H. Li, Z. Jiang, L. Dong, X. Kan, H. Yang, A. Li, R. Cheng, Removal of dyes from aqueous solutions by straw based adsorbents: batch and column studies, *Chem. Eng. J.* 168 (2011) 1120–1127.
- [7] W.S.W. Ngah, L.C. Teong, M.A.K.M. Hanafiah, Adsorption of dyes and heavy metal ions by chitosan composites: a review, *Carbohydr. Polym.* 83 (2011) 1446–1456.
- [8] R. Gong, R. Guan, J. Zhao, X. Liu, S. Ni, Citric acid functionalizing wheat straw as sorbent for copper removal from aqueous solution, *J. Health Sci.* 54 (2008) 174–178.
- [9] E. Pehlivan, T. Altun, S. Parlayici, Modified barley straw as a potential biosorbent for removal of copper ions from aqueous solution, *Food Chem.* 135 (2012) 2229–2234.
- [10] S. Chowdhury, S. Chakraborty, P. Das, Adsorption of crystal violet from aqueous solution by citric acid modified rice straw: equilibrium, kinetics, and thermodynamics, *Sep. Sci. Technol.* 48 (2013) 1339–1348.
- [11] B. Ramaraju, P.M.K. Reddy, C. Subrahmanyam, Low cost adsorbents from agricultural waste for removal of dyes, *Environ. Prog. Sustain. Energy* 33 (2014) 38–46.
- [12] I. Safarik, M. Safarikova, Magnetic fluid modified peanut husks as an adsorbent for organic dyes removal, *Phys. Proc.* 9 (2010) 274–278.
- [13] I. Safarik, K. Horska, B. Svobodova, M. Safarikova, Magnetically modified spent coffee grounds for dyes removal, *Eur. Food Res. Technol.* 234 (2012) 345–350.
- [14] L.S. Oliveira, A.S. Franca, T.M. Alves, S.D.F. Rocha, Evaluation of untreated coffee husks as potential biosorbents for treatment of dye contaminated waters, *J. Hazard. Mater.* 155 (2008) 507–512.
- [15] I. Safarik, K. Horska, M. Safarikova, Magnetically modified spent grain for dye removal, *J. Cereal Sci.* 53 (2011) 78–80.
- [16] S.T. Ong, P.S. Keng, S.T. Ooi, Y.T. Hung, S.L. Lee, Utilization of fruits peel as a sorbent for removal of methylene blue, *Asian J. Chem.* 24 (2012) 398–402.
- [17] C.B. Chandran, D. Singh, P. Nigam, Remediation of textile effluent using agricultural residues, *Appl. Biochem. Biotechnol.* 102 (2002) 207–212.
- [18] H. Deveci, E. Pehlivan, The utilization of modified rye straws as biosorbents for Cr (VI) ions [online], in: *Proceedings of the 2nd International Symposium on Sustainable Development*, 2010. Available from: <http://eprints.ibu.edu.ba/445>.
- [19] W. Kaminski, E. Tomczak, S. Kuberski, Sorption equilibrium of selected azo dyes onto low-cost sorbents, *Glob. J. Adv. Pure Appl. Sci.* 1 (2013) 94–100.
- [20] C.T. Yavuz, A. Prakash, J.T. Mayo, V.L. Colvin, Magnetic separations: from steel plants to biotechnology, *Chem. Eng. Sci.* 64 (2009) 2510–2521.
- [21] I. Safarik, M. Safarikova, One-step magnetic modification of non-magnetic solid materials, *Int. J. Mater. Res.* 105 (2014) 104–107.
- [22] L. Sun, B. Fugetsu, Graphene oxide captured for green use: influence on the structures of calcium alginate and macroporous alginic beads and their application to aqueous removal of acridine orange, *Chem. Eng. J.* 240 (2014) 565–573.
- [23] S.K.H. Nejad-Darzi, A. Samadi-Maybodi, M. Ghobakhloo, Synthesis and characterization of modified ZSM-5 nanozeolite and their applications in adsorption of acridine orange dye from aqueous solution, *J. Porous Mater.* 20 (2013) 909–916.
- [24] S. Qadri, A. Ganoe, Y. Haik, Removal and recovery of acridine orange from solutions by use of magnetic nanoparticles, *J. Hazard. Mater.* 169 (2009) 318–323.
- [25] I. Safarik, L.F.T. Rego, M. Borovska, E. Mosiniewicz-Szablewska, F. Weyda, M. Safarikova, New magnetically responsive yeast-based biosorbent for the efficient removal of water-soluble dyes, *Enzyme Microb. Technol.* 40 (2007) 1551–1556.
- [26] I. Safarik, M. Safarikova, F. Weyda, E. Mosiniewicz-Szablewska, A. Slawska-Waniewska, Ferrofluid-modified plant-based materials as adsorbents for batch separation of selected biologically active compounds and xenobiotics, *J. Magn. Magn. Mater.* 293 (2005) 371–376.
- [27] A.A. Farghali, M. Bahgat, W.M.A. El Rouby, M.H. Khedr, Preparation, decoration and characterization of graphene sheets for methyl green adsorption, *J. Alloys Compd.* 555 (2013) 193–200.
- [28] J. Liu, Y. Su, Q. Li, Q. Yue, B. Gao, Preparation of wheat straw based superabsorbent resins and their applications as adsorbents for ammonium and phosphate removal, *Bioresour. Technol.* 143 (2013) 32–39.
- [29] X.-F. Sun, Z. Jing, H. Wang, Y. Li, Removal of low concentration Cr(VI) from aqueous solution by modified wheat straw, *J. Appl. Polym. Sci.* 129 (2013) 1555–1562.
- [30] W. Zhang, H. Li, X. Kan, L. Dong, H. Yan, Z. Jiang, H. Yang, A. Li, R. Cheng, Adsorption of anionic dyes from aqueous solutions using chemically modified straw, *Bioresour. Technol.* 117 (2012) 40–47.
- [31] F. Batzias, D. Sidiras, E. Schroeder, C. Weber, Simulation of dye adsorption on hydrolyzed wheat straw in batch and fixed-bed systems, *Chem. Eng. J.* 148 (2009) 459–472.
- [32] B.C. Oei, S. Ibrahim, S. Wang, H.M. Ang, Surfactant modified barley straw for removal of acid and reactive dyes from aqueous solution, *Bioresour. Technol.* 100 (2009) 4292–4295.
- [33] X. Xu, Y. Gao, B. Gao, Q. Yue, Q. Zhong, Adsorption studies of the removal of anions from aqueous solutions onto an adsorbent prepared from wheat straw, *Sci. China Chem.* 53 (2010) 1414–1419.
- [34] R. Han, L. Zhang, C. Song, M. Zhang, H. Zhu, L. Zhang, Characterization of modified wheat straw, kinetic and equilibrium study about copper ion and methylene blue adsorption in batch mode, *Carbohydr. Polym.* 79 (2010) 1140–1149.
- [35] M. Sciban, M. Klasnja, B. Skrbic, Adsorption of copper ions from water by modified agricultural by-products, *Desalination* 229 (2008) 170–180.
- [36] A. Kumar, N.N. Rao, S.N. Kaul, Alkali-treated straw and insoluble straw xanthate as low cost adsorbents for heavy metal removal – preparation, characterization and application, *Bioresour. Technol.* 71 (2000) 133–142.
- [37] R. Chand, T. Watari, K. Inoue, T. Torikai, M. Yada, Evaluation of wheat straw and barley straw carbon for Cr(VI) adsorption, *Sep. Purif. Technol.* 65 (2009) 331–336.
- [38] X. Li, Y. Liu, M.Z. Hua, Y. Liu, Z. Zhang, X. Li, C. He, Adsorption of U(VI) from aqueous solution by cross-linked rice straw, *J. Radioanal. Nucl. Chem.* 298 (2013) 383–392.
- [39] S.-T. Song, N. Saman, K. Johari, H. Mat, Removal of Hg(II) from aqueous solution by adsorption using raw and chemically modified rice straw as novel adsorbents, *Ind. Eng. Chem. Res.* 52 (2013) 13092–13101.
- [40] X.F. Sun, R.C. Sun, J.X. Sun, Acetylation of rice straw with or without catalysts and its characterization as a natural sorbent in oil spill cleanup, *J. Agric. Food Chem.* 50 (2002) 6428–6433.