Sunflower seed shells: A novel and effective low-cost adsorbent for the removal of the diazo dye Reactive Black 5 from aqueous solutions

Johann F. Osma, Verónica Saravia, José L. Toca-Herrera, Susana Rodríguez Couto *

Department of Chemical Engineering, Rovira i Virgili University, Av. Països Catalans 26, 43007 Tarragona, Spain

Abstract

In this paper, the potential of two low-cost adsorbents such as sunflower seed shells (SS) and mandarin peelings (MP) in the removal of the synthetic anionic dye Reactive Black 5 (RB5) from aqueous solutions was investigated. SS led to a percentage of dye removal higher than MP (85% and 71% after 210 min, respectively, for an initial RB5 concentration of $50 \, mg \, L^{-1}$ and an initial pH of 2.0).

The rate of adsorption followed a pseudo-second-order kinetic model and the intra-particle diffusion was found to be the rate-controlling stage. In addition, the equilibrium data fitted well both the Freundlich and multilayer adsorption isotherm equations indicating the heterogeneity of the adsorbent surface. This was also corroborated by the SEM photographs. On the whole, the results in this study indicated that SS were very attractive materials for removing anionic dyes from dyed effluents.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Adsorption isotherms; Adsorption kinetics; Intra-particle diffusion; Mandarin peelings; Pseudo-second-order kinetics; Reactive Black 5; Sunflower seed shells

1. Introduction

Azo dyes are synthetic organic compounds widely used in textile dyeing, paper printing and other industrial processes such as the manufacture of pharmaceutical drugs, toys and foods including candies. This chemical class of dyes, which is characterised by the presence of at least one azo bond (–N=N–) bearing aromatic rings, dominates the world-wide market of dyestuffs with a share of about 70% [1]. These dyes are highly recalcitrant to conventional wastewater treatment processes. In fact, as much as 90% of reactive azo dyes could remain unaffected after activated sludge treatment [2]. Therefore, alternative methods should be implemented for effective treatment of dyed effluents.

There are five main methods used for the treatment of dye-containing effluents: adsorption, oxidation–ozonation, biological treatment, coagulation–flocculation and membrane process [3]. Adsorption process is noted to be superior to other removal techniques because it is more economical, simpler [4] and it is capable to efficiently treat dyes in a more concentrated form [5].

Activated carbon [6,7] is the most popular and widely used dye adsorbent but it suffers from several drawbacks such as its high price of both manufacturing and regeneration and it is ineffective against disperse and vat dyes. This has impelled the search for cheaper substitutes like the solid wastes generated from the agricultural industry. The accumulation and concentration of pollutants from aqueous solutions by the use of biological materials is named bio-adsorption. The bio-adsorbents are often much more selective than traditional ion-exchange resins and commercial activated carbons and can reduce dye concentration to ppb levels.

The aim of this study was to investigate the potential of two wastes of the agricultural industry such as mandarin peelings (MP) and sunflower seed shells (SS) as bio-adsorbents in the removal of the synthetic diazo dye Reactive Black 5 (RB5) from aqueous solutions. To the best of our knowledge SS have not been used as dye adsorbents before this study.

2. Materials and methods

2.1. Adsorbents

Mandarin (*Citrus reticulata*) peelings (MP) were obtained from a local market, cut into small pieces, washed to remove
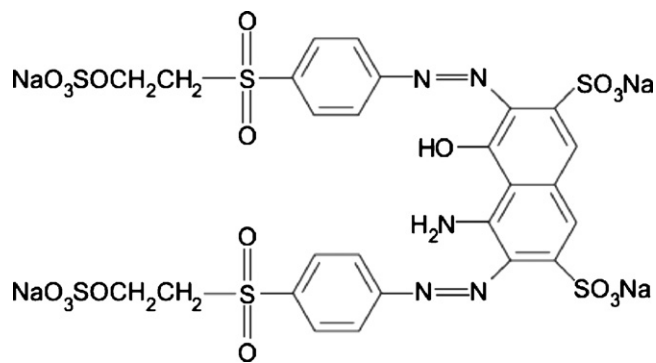

Fig. 1. Molecular structure of the dye Reactive Black 5 (RB5).

any adhering dirt, air dried at room temperature for 36 h and milled (particle sized about 0.4 mm). The chemical composition of the MP was 32–34% soluble carbohydrates, 12–14% cellulose, 11–14% reducing substances, 9–11% lignin and 1.1–1.3% total nitrogen [8]. MP had a mean pore area of 231.73 μm^2.

Sunflower (*Helianthus annuus*) seed shells (SS) were obtained from a local market, washed to remove any adhering dirt and air dried at room temperature for 36 h. The chemical composition of the SS was 31.9% cellulose, 29.3% lignin and 27.2% pentosan [9]. SS showed a mean surface area of 1.55 cm^2 and a mean pore area of 244.98 μm^2.

2.2. Reagents and solutions

The anionic diazo dye Reactive Black 5 (CI 20505) was purchased from Sigma–Aldrich (St. Louis, MO, USA) and was used without any further purification. The chemical structure of this dye is shown in Fig. 1. Distilled water was used as a solvent. The solutions contained different dye concentrations and pH was adjusted to 2.0 and 4.0 by adding a small amount of 2 M H$_2$SO$_4$.

2.3. Adsorption procedure

The adsorption processes were conducted at room temperature by mixing 4 g of milled MP or 4 g of SS in 250 mL-Erlenmeyer flasks containing 100 mL of aqueous solutions at different concentrations of the dye RB5 at pH 2.0 and 4.0 and 100 rpm (Orbital shaker, Ovan, Lovango SL, Spain), according to the experiment. The changes in absorbance were determined spectrophotometrically (Perkin-Elmer, CA, USA) at certain time intervals during the adsorption processes at a wavelength of 597 nm, which corresponds to the maximum adsorption peak of RB5, or measuring the area under the plot from 400 to 750 nm. Decolouration was expressed in terms of percentage. The experiments were performed three times, the experimental error being around 4% (mean value)

2.4. Microscopic examination

Original and dyed SS samples were sputter coated with gold and examined with a Jeol 6400 scanning electron microscope (SEM) at 15 kV, belonging to SRCiT (Scientific and Technical Services) of the Rovira i Virgili University (Tarragona, Spain).

3. Results and discussion

3.1. Effect of the adsorbent on dye removal

As shown in Fig. 2 the adsorption rate of MP was faster than that of SS for the first stages of the process; however SS led to a higher percentage of RB5 removal for 50 min onwards. Thus, in 210 min (equilibrium time) SS showed an adsorption percentage of 85% and MP of 71%. In addition, the SS-based process showed the following advantages over the MP-based one: the resulting aqueous solution was nearly colourless and SS milling was not necessary. This would reduce the cost of the overall process. Therefore, SS were selected for performing the subsequent experiments.

3.2. Effect of initial dye concentration and initial pH on dye adsorption

Adsorption of RB5 from aqueous solutions onto SS was measured at given contact times for three different initial dye concentrations (15, 30 and 50 mg L^{-1}) at an adsorbent dose of 4 g. The effect of the initial dye concentration on the rate of adsorption is shown in Fig. 3A. The percentage of dye adsorbed increased as the initial dye concentration decreased for the first 30 min. Afterwards, the dye adsorption was higher for 30 and 50 mg L^{-1} of initial dye concentration. The time taken to reach equilibrium was equal for all the initial dye concentrations used, which was 210 min. This finding is supported by the study carried out by Poots et al. [10], who reported that the initial concentration of dyes had only a small influence on the time of contact necessary to reach equilibrium in the adsorption study of Telon Blue by peat.

Solution pH affects both aqueous chemistry and surface binding-sites of the adsorbents. The effect of initial pH on adsorption percentages of RB5 was studied at pHs 2 and 4. As shown in Fig. 3A and B, the dye removal ratio was minimal at the initial pH 4, especially for initial RB5 concentrations of 30 and 50 mg L^{-1}. This could be attributed to the adsorption
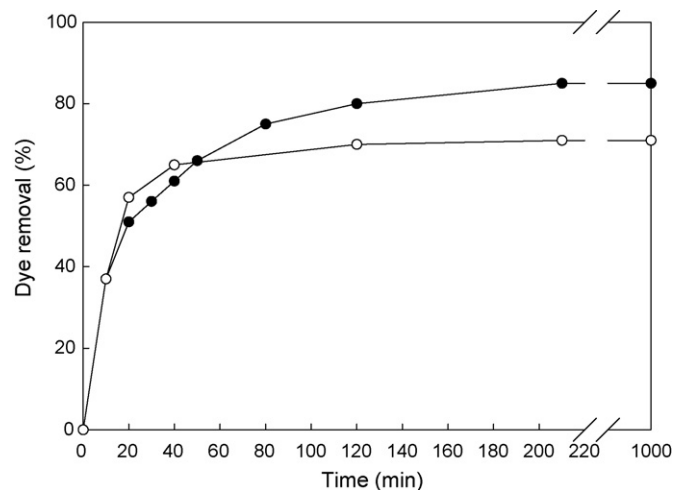

Fig. 2. Percentage of RB5 removal for SS ($\bullet$) and MP ($\bigcirc$) (pH 2; C_0, 50 mg L^{-1}).
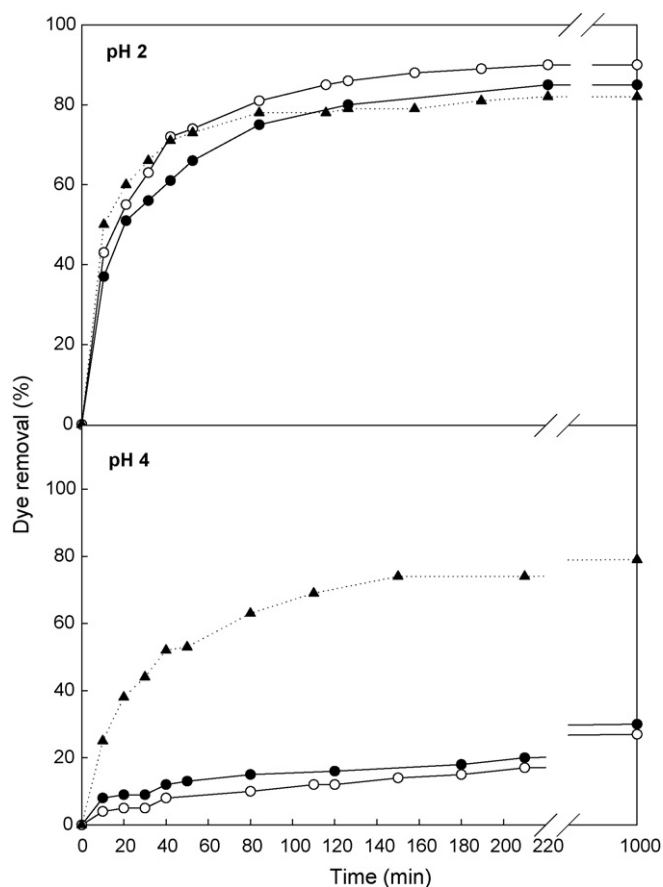
Fig. 3. Percentage of RB5 removal for SS at different pHs: (A) pH 2 and (B) pH 4 and at different initial RB5 concentrations: (●) 50 mg L^{-1}; (○) 30 mg L^{-1}; (▲) 15 mg L^{-1}.

of dye molecules onto SS was driven by the electrostatic attraction between adsorbed H^{+} groups and the anionic dye. Since the SS are negatively charged, the repulsion between the anionic dye and the negatively charged SS surface will be enhanced with an increase in pH, thereby decreasing the binding strength.

Our results are in agreement with those reported by Sivaraj et al. [11], who found that the removal of Acid Violet 17 by orange peels was maximal at pH 2. More recently, Gong et al. [12] also reported that the removal of three anionic dyes by powdered peanut hull was maximal at pH 2.

According to the above results pH 2 was selected for performing the subsequent experiments.

3.3. Kinetics of the adsorption process

Fig. 4A illustrates the adsorption kinetics of RB5. The removal rate of RB5 was very fast during the initial stages of the adsorption processes, especially for an initial dye concentration of 30 mg L^{-1}. However, the adsorption equilibrium was reached at 210 min for all the three concentrations tested. The kinetic data in Fig. 4A were treated with a pseudo-second-order rate equation. The second-order kinetic model [13,14] is expressed as:
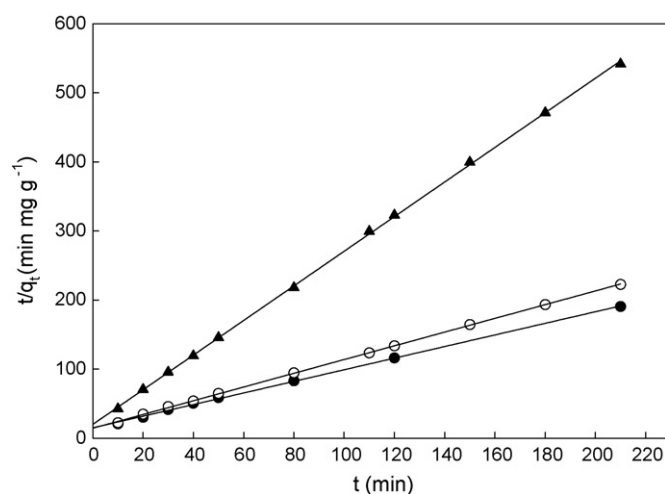

Fig. 4. Pseudo-second-order adsorption kinetics of RB5 on SS at pH 2 and different initial RB5 concentrations: (●) 50 mg L^{-1}; (○) 30 mg L^{-1}; (▲) 15 mg L^{-1}.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

where k_2 is the pseudo-second-order rate constant (g mg^{-1} min^{-1}); q_e the quantity of dye adsorbed at equilibrium (mg g^{-1}); q_t the quantity of dye adsorbed at time t (mg g^{-1}) and t is the time (min).

As shown in Fig. 4 the data fitted well with the second order kinetics model ($R^2 > 0.999$). Also, the calculated q_e values agree very well with the experimental data (Table 1). Similar kinetic results were reported in the biosorption of Reactive Black 5 by powdered active carbon (PAC) and fly ash [13].

3.4. Intra-particle diffusion study

The intra-particle diffusion model [14] was applied to describe the dye adsorption. Assuming that the rate is controlled by pore and intra-particle diffusion, in a non-flow-agitated system, the amount adsorbed (q_t) is proportional to the square root of time ($t^{1/2}$), as per the relationship given by Weber and Moris [14].

$$q_t = k_p t^{1/2}$$

where q_t (mg g^{-1}) is the adsorbate uptake at time t (min); k_p (mg g^{-1} min$^{-1/2}$) is the intra-particle diffusion rate constant.

The plot of q_t *versus* $t^{1/2}$ may present multi linearity [15], which indicates that two or more steps occur in the adsorption processes. The first sharper portion is the external surface

Table 1
Pseudo-second-order adsorption rate constants and calculated and experimental q_e values for different initial RB5 concentrations at pH 2

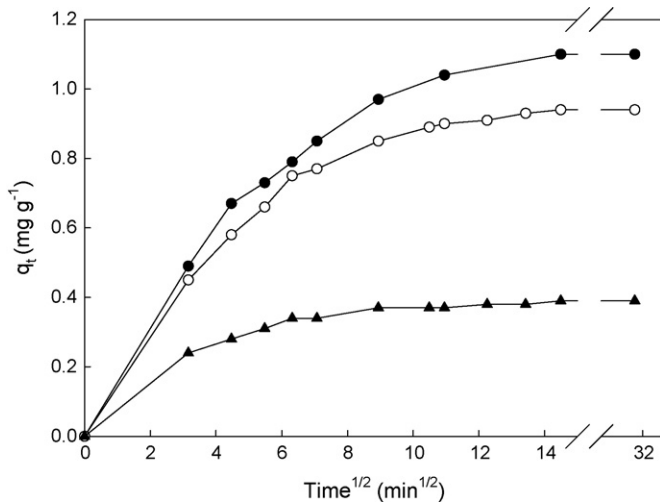| RB5 (mg L^{-1})	K_2 (g mg^{-1} min^{-1})	q_e calc. (mg g^{-1})	q_e exp. (mg g^{-1})	R^2
15	0.314	0.40	0.39	0.9998
30	0.047	1.19	0.94	0.9991
50	0.069	1.01	1.10	0.9998

Fig. 5. Intra-particle diffusion plot for RB5 adsorption by SS at pH 2 and different initial RB5 concentrations: (●) 50 mg L^{-1}; (○) 30 mg L^{-1}; (▲) 15 mg L^{-1}.

adsorption or instantaneous adsorption stage. The second portion is the gradual adsorption stage, where the intra-particle diffusion is rate-controlled. The third portion is the final equilibrium stage, where the intra-particle diffusion starts to slow down due to the extremely low solute concentration in solution [16]. Fig. 5 shows the plot of q_t versus $t^{1/2}$. The slope of the line in each stage is written as the rate parameter $k_{p,i}$ ($i = 1$–3). The corresponding rate parameters are listed in Table 2.

Fig. 5 indicates that two linear stages are involved with a rapid diffusion rate in the initial stage at higher RB5 concentrations. The lines pass through the origin, indicating that intra-particle diffusion is the rate-controlling step of the adsorption process. So, predominantly, adsorption of RB5 took place rapidly by external mass transfer followed by intra-particle diffusion. The value of the rate constants for intra-particle transport ($k_{p,1}$, $k_{p,2}$ and $k_{p,3}$) increased with the increase in the initial RB5 concentration (Table 2).

3.5. Adsorption isotherms

The equilibrium data were fitted into Freundlich and multilayer adsorption equations to determine the correlation between the isotherm models and experimental data.

3.5.1. Freundlich isotherm

The Freundlich isotherm is an empirical model that considers heterogeneous adsorptive energies on the adsorbent surface. It

Table 2
Intra-particle diffusion rate constants for different initial RB5 concentrations at pH 2

RB5 (mg L^{-1})	$k_{p,1}$ (g mg^{-1} min$^{-1/2}$)	$k_{p,2}$ (g mg^{-1} min$^{-1/2}$)	$k_{p,3}$ (g mg^{-1} min$^{-1/2}$)
15	0.082	0.0146	0.0039
30	0.1267	0.0515	0.0164
50	0.1416	0.0687	0.024

Table 3
Freundlich constants and calculated and experimental q_e values for different initial RB5 concentrations at pH 2

RB5 (mg L^{-1})	q_e calc. (mg g^{-1})	q_e exp. (mg g^{-1})	k_F	n	R^2
10	0.17030	0.1875	0.0376	0.6061	0.9553
20	0.4826	0.3825			
30	0.6444	0.6100			
40	0.7826	0.8425			
50	0.9532	1.0725			

is expressed by the following equation:

$$q_e = k_F C_e^{1/n}$$

where q_e (mg g^{-1}) is the amount of dye adsorbed at equilibrium, C_e (mg L^{-1}) the dye concentration at equilibrium and k_F and n are the Freundlich constants for the system, which are indicators of adsorption capacity and intensity, respectively [17].

To determine the constants k_F and n the linear form of the equation is used:

$$\ln q_e = \ln k_F + \frac{1}{n} \ln C_e$$

The plot of $\ln q_e$ versus $\ln C_e$ is employed to generate the intercept K_F and the slope $1/n$. The values of K_F, n, the experimental and the calculated q_e (mg g^{-1}) values and the linear regression correlation (R^2) for Freundlich are given in Table 3. The value of $1/n > 1$ indicates that saturation was not attained [18]. The fit of the data to the Freundlich equation indicates the heterogeneity of the adsorbent surface.

3.5.2. Multilayer adsorption isotherm

The multilayer adsorption isotherm model described by Wang et al. [19] was also used to describe the experimental adsorption data. The model is expressed by the following equation:

$$q_e = \frac{Q_m K_1 C_e}{(1 - K_2 C_e)[1 + (K_1 - K_2)C_e]}$$

where q_e (mg g^{-1}) is the amount of dye adsorbed at equilibrium, Q_m (mg g^{-1}) the maximum monolayer adsorption capacity, C_e (mg L^{-1}) the dye concentration at equilibrium, K_1 the equilibrium constant for the first layer adsorption and K_2 is the equilibrium constant for multilayer adsorption.

Writing the above equation in another way and regrouping terms:

$$\frac{C_e}{q_e} = \frac{C_e^2(K_2^2 - K_1 K_2) + C_e(K_1 - 2K_2) + 1}{Q_m K_1}$$

Plotting C_e/q_e versus C_e and adjusting to a second-order polynomial equation Q_m, K_1 and K_2 are obtained. The values of Q_m, K_1, K_2, the experimental and the calculated q_e (mg g^{-1}) values and the linear regression correlation (R^2) are given in Table 4. The calculated q_e values agree quite well with the experimental ones. It can be seen that the multilayer adsorption constant is much lower than that of the first layer.

Table 4
Multilayer model constants and calculated and experimental q_e values for different initial RB5 concentrations at pH 2

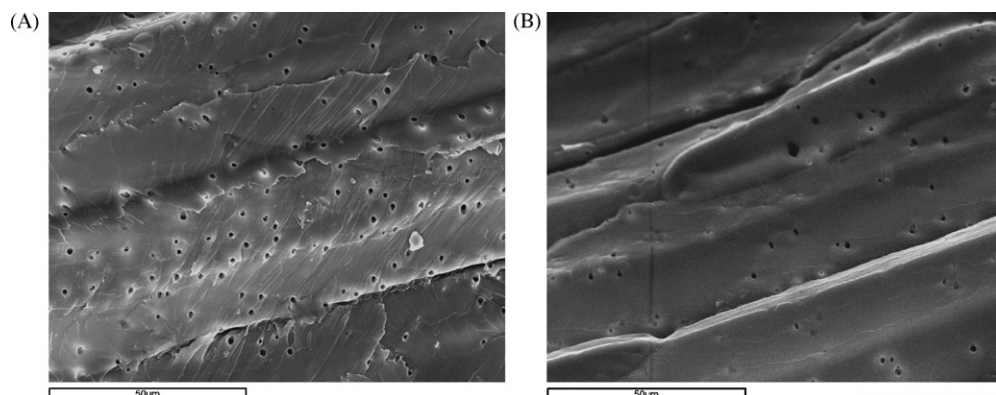| RB5 (mg L^{-1})	q_e calc. (mg g^{-1})	q_e exp. (mg g^{-1})	Q_m (mg g^{-1})	k_1 (L mg^{-1})	k_2 (L mg^{-1})	R^2
10	0.1852	0.1875	0.873	0.8977	0.00688	0.9425
20	0.4133	0.3825				
30	0.5743	0.6100				
40	0.7693	0.8425				
50	1.1676	1.0725				

Fig. 6. SEM photographs of the SS: (A) original and (B) at the end of the adsorption process.

3.6. SEM photographs

Fig. 6A and B show the SEM photographs of the original and the dyed SS, respectively. SS has heterogeneous surface and macro-pores as seen from its SEM photograph. After RB5 adsorption, SS presents a smoother surface because of the packing of the dye what makes surface irregularities less sharp.

4. Conclusions

Sunflower seeds shells, which are discarded as waste material from the food industry, are promising bio-adsorbents for the removal of dyes from aqueous solutions. Hence, in the present study their potential to adsorb an anionic dye in extremely acidic conditions (pH 2) was shown. The dyed SS have potential to be used as substrates in solid state fermentation (SSF). Thus, degradation of the adsorbed dye takes place whilst simultaneously enriching the protein content of the substrate by the presence of fungal biomass. The fermented mass can be utilised as a fertiliser or a soil conditioner. Another alternative is to burn the dyed SS to generate power. The utilisation of this waste would contribute to the so-called green biotechnology.

Acknowledgements

References

[1] G.M.B. Soares, M.T.P. Amorim, R. Hrdina, M. Costa-Ferreira, Studies on the biotransformation of novel diazo dyes by laccase, Process Biochem. 37 (2002) 581–587.
[2] J. Pierce, Colour in textile effluents—the origins of the problem, J. Soc. Dyers Colour. 110 (1994) 131–134.
[3] G.M. Walker, L. Hansen, J.A. Hana, S.J. Allen, Kinetics of a reactive dye adsorption onto dolomitic sorbents, Water Res. 37 (2003) 2081–2089.
[4] L.S. Tsui, W.R. Roy, M.A. Cole, Removal of dissolved textile dyes from wastewater by a compost sorbent, Color. Technol. 119 (2003) 14–18.
[5] G. Annadurai, R.S. Juang, D.J. Lee, Factorial design analysis for adsorption of dye on activated carbon beads incorporated with calcium alginate, Adv. Environ. Res. 6 (2002) 191–198.
[6] K.C.L.N. Rao, K.K. Ashutosh, Color removal from dyestuff industry effluent using activated carbon, Indian J. Chem. Techn. 1 (1994) 13–19.
[7] S.J. Allen, Types of adsorbent materials, in: G. McKay (Ed.), Use of Adsorbents for the Removal of Pollutants from Wastewaters, CRC Inc., Boca Raton, FL, USA, 1996, pp. 59–97.
[8] M. Stajić, L. Persky, D. Friesem, Y. Hadar, S.P. Wasser, E. Nevo, J. Vukojević, Effect of different carbon and nitrogen sources on laccase and peroxidases production by selected *Pleurotus* species, Enzyme Microb. Tech. 38 (2006) 65–73.
[9] M.V. Efanov, A.G. Klepikov, Preparation of N-containing lignocarbohydrates, Chem. Nat. Comp. 37 (2001) 80–82.
[10] V.J.P. Poots, G. McKay, J.J. Healy, The removal of acid dye from effluent using natural adsorbents. I. Peat, Water Res. 10 (1976) 1067–1070.
[11] R. Sivaraj, C. Namasivayam, K. Kadirvelu, Orange peel as an adsorbent in the removal of Acid violet 17 (acid dye) from aqueous solutions, Waste Manage. 21 (2001) 105–110.
[12] R. Gong, Y. Ding, M. Li, C. Yang, H. Liu, Y. Sun, Utilization of powdered peanut hull as biosorbent for removal of anionic dyes from aqueous solution, Dyes Pigments 64 (2005) 187–192.
[13] Z. Eren, F.N. Acar, Adsorption of Reactive Black 5 from an aqueous solution: equilibrium and kinetic studies, Desalination 194 (2006) 1–10.

[14] W.J. Weber, J.C. Morris, Advances in water pollution research: removal of bio-logically resistant pollutants from waste waters by adsorption, International Conference on Water Pollution Symposium, vol. 2, Pergamon, Oxford, 1962, pp. 231–266.

[15] S.J. Allen, G. Mckey, K.Y.H. Khadur, Intraparticle diffusion of basic dye during adsorption on to sphagnum peat, Environ. Pollut. 56 (1989) 39–42.

[16] M.-S. Chiou, G.-S. Chuang, Competitive adsorption of dye metanil yellow and RB15 in acid solutions on chemically cross-linked chitosan beads, Chemosphere 62 (2006) 731–740.

[17] Z. Aksu, D. Dönmez, A comparative study on the biosorption characteristics of some yeasts for Remazol Blue reactive dye, Chemosphere 50 (2003) 1075–1083.

[18] M.M. Dávila-Jiménez, M.P. Elizalde-González, A.A. Peláez-Cid, Adsorption interaction between natural adsorbents and textile dyes in aqueous solution, Colloids Surface A Physicochem. Eng. Aspect 254 (2005) 107–114.

[19] J. Wang, C.P. Huang, H.E. Allen, D.K. Cha, D.-W. Kim, Adsorption characteristics of dye onto sludge particulates, J. Colloid Interface Sci. 208 (1998) 518–528.