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ScienceDirect
Dyes and Pigments 73 (2007) 332–337
DYES and PIGMENTS
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Removal of basic dyes from aqueous solution by sorption on phosphoric acid modified rice straw

Renmin Gong [a,b,*], Youbin Jin [a], Jian Chen [b], Yun Hu [a], Jin Sun [a]

[a] College of Life Science, Anhui Normal University, Wuhu 241000, PR China
[b] School of Biotechnology, Southern Yangtze University, Wuxi 214036, PR China

Received 7 December 2005; accepted 7 January 2006
Available online 20 March 2006

Abstract

In this article, rice straw was chemically modified by means of phosphorylation, and then the phosphoric acid modified rice straw was further loaded with sodium ion in order to yield potentially biodegradable cationic sorbent. The feasibility of the modified product as cationic dye sorbent for removing basic dyes from aqueous solution was investigated. Two basic dyes, basic blue 9 (BB9) and basic red 5 (BR5), were used as sorbates. The effects of various experimental parameters (e.g. initial pH, sorbent dosage, dye concentration, ion strength, contact time) were examined and optimal experimental conditions were decided. The BB9 and BR5 removal ratios came up to the maximum value beyond pH 4. The 1.5 g/l or more sorbent could almost completely remove BB9 and BR5 from 250 mg/l of dye solution. The ratios of BB9 and BR5 sorbed were kept above 96% over a range from 50 to 350 mg/l of dye concentration when 2.0 g/l of sorbent was used. Increase in ion strength of solution induced decline of BB9 and BR5 sorption. The isothermal data fitted the Langmuir model. The sorption processes followed the pseudo-first-order rate kinetics. The results in this research confirmed that the phosphoric acid modified rice straw was an excellent basic dye sorbent.

Keywords: Sorption; Basic blue 9; Basic red 5; Chemical modification; Phosphoric acid; Rice straw

1. Introduction

The fact that synthetic dyes are largely used in many industries presents certain hazards and environmental problems. Today there are more than 10,000 dyes with different chemical structures available commercially [1]. Color in waterbody is not only aesthetically unpleasant but also interferes light penetration and reduces photosynthetic action. Many dyes or their metabolites have toxic as well as carcinogenic, mutagenic and teratogenic effects on aquatic life and humans [2,3].

Some biological and physical/chemical methods have been employed for dye wastewater treatment. These methods include anaerobic/aerobic treatment [4,5], coagulation/flocculation [6], oxidation/ozonation [7,8], membrane separation [9] and sorption [10]. Activated carbon as a sorbent has been used for decades to remove contaminants from industrial wastewater. Although regenerative, high operating costs and problems with regeneration hamper large-scale application of activated carbon.

Agricultural by-products are considered to be low value products. Because of low utilization ratio, most of these biomaterials are arbitrarily discarded or set on fire. These disposals must result in resource loss and environmental pollution. The exploitation and utilization of these biomaterials must bring obvious economic and social benefits to mankind. In recent years, attention has been focused on the utilization of native agricultural by-products as sorbent [11–18]. Generally, the sorption capacity of native agricultural by-products is low. In order to improve the sorption capacity of these biomaterials, the agricultural by-products were chemically modified with different reagents and methods [19–22].

* Corresponding author. College of Life Science, Anhui Normal University, Wuhu 241000, PR China. Tel.: +86 553 5991085.
E-mail address: rmgong.nju@163.com (R. Gong).

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doi:10.1016/j.dyepig.2006.01.037

Rice straw is a lignocellulosic agricultural by-product containing cellulose (37.4%), hemi-cellulose (44.9%), lignin (4.9%) and silicon ash (13.1%) [23]. In China, about 200 billion kilograms of rice straw are produced annually as a by-product of rice production. The disposal of rice straw by open-field burning frequently causes serious air pollution, hence new economical technologies for rice straw disposal and utilization must be developed. In this paper, rice straw was chemically modified by means of phosphorylation, and then the phosphoric acid modified rice straw was further loaded with sodium ion in order to yield potentially biodegradable cationic sorbent. The feasibility of the modified product as cationic dye sorbent for removing basic dyes from aqueous solution was investigated. The objectives of this work were: (1) to convert rice straw to a new cationic sorbent with high sorption capacity, and (2) to examine potential application of this new sorbent in basic dye wastewater treatment.

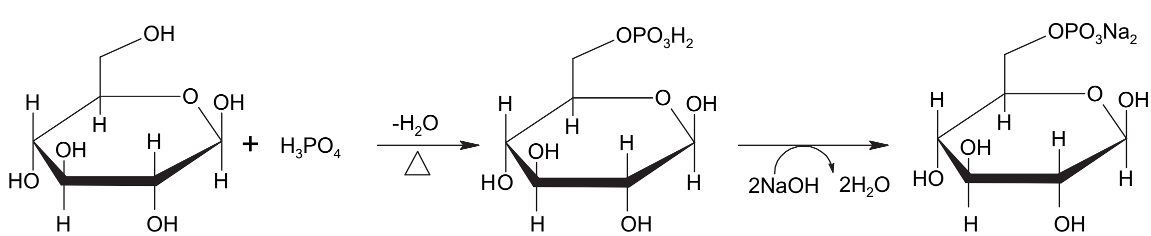
2. Materials and methods

2.1. Preparation of modified sorbent

Rice straw was collected from a local farm. The collected biomaterial was cut into segment of 10 cm length and washed with tap water to remove soil and dust, and then dried overnight at 50 °C. Dried rice straw segment was ground and sieved to retain the 20–40 mesh fraction for further chemical modification.

The chemical modification of rice straw was made according to a similar method previously described by the literature [24]. Ground rice straw (5.43 g) was soaked in 200 ml of dimethyl formamide (DMF) overnight and the dirty DMF was removed by vacuum filtration. The residua, again immersed in 200 ml of fresh DMF was placed in a flask along with 5.04 g of urea, and the mixture was stirred using a magnetic stirrer and 3.10 g of phosphoric acid (PA) were added dropwise while stirring. After 1 h stirring, the temperature of the reaction mixture was raised to 150 °C and further stirred for 2 h. After cooling to room temperature and filtration, the reactant was washed with 70% ethanol and then with water to neutral pH. After that, the wet PA-modified rice straw was suspended in 0.1 M NaOH at suitable ratio and stirred for 60 min, followed by washing thoroughly with distilled water to remove residual alkali, and then the wet product was dried at 50 °C for 24 h and preserved in a desiccator for further use as sorbent.

The chemical modification of rice straw can be schematically expressed by equation:



2.2. Preparation of basic dye solution

Two basic dyes of commercial purity, basic blue 9 (BB9) and basic red 5 (BR5), were used without further purification. BB9 is a basic dye of phenothiazine type (C.I. No 52015, FW = 373.9, $\lambda_{max} = 670$ nm) and BR5 is a basic dye of phenazine type (C.I. No 50040, FW = 288.8, $\lambda_{max} = 530$ nm). The dye stock solutions were prepared by dissolving accurately weighted dyes in distilled water to the concentration of 500 mg/l. The experimental solutions were obtained by diluting the dye stock solutions in accurate proportions to different initial concentrations.

2.3. Experimental methods and measurements

Sorption experiments were carried out in a rotary shaker at 150 rpm and at ambient temperature (20 ± 2° C) using 250-ml shaking flasks containing 100 ml different concentrations and initial pH values of dye solution. The initial pH values of the solution were previously adjusted with 0.1 M HNO_3 or NaOH using pH meter. Different doses of sorbent were added to each flask. After shaking the flasks for predetermined time intervals, the samples were withdrawn from the flasks and the dye solutions were separated from the sorbent by sedimentation/centrifugation. Dye concentrations in the supernatant solutions were estimated by measuring absorbance at maximum wavelengths of dyes with a 752W Grating Spectrophotometer (Shanghai, China) and computing from the calibration curves.

The experiments were conducted in duplicate and the negative controls (with no sorbent) were simultaneously carried out to ensure that sorption was by sorbent and not by the container.

2.4. Determination of total phosphorus

The molybdenum blue method was employed for spectrophotometric determination of total phosphorus in raw and PA-modified rice straw.

Samples of raw and PA-modified rice straw were digested as follows: 0.100 g of MgO and samples (0.0100 g for PA-modified rice straw and 0.1000 g for raw rice straw) were weighed in quartz crucible, placed in a furnace and incinerated at 800 °C. Blank digestion was also carried out in the same way.

After incinerated, the samples were dissolved in 20 ml of redistilled water containing 20 ml of 1 M H_2SO_4, and then transferred into 100-ml volumetric flask, followed by the addition of ammonium molybdate (5.30×10^{-3} M) and hydrazine sulphate (3.07×10^{-3} M) in 20 ml and heated in boiling water bath for 20 min. After cooling, the solution was made up to the mark and the absorbance was measured at 730 nm against a reagent blank.

The total phosphorus content in sample was derived from calibration curve that was obtained using standard solution of KH_2PO_4 in same spectrophotometric analytical condition.

3. Results and discussion

3.1. Influence of initial pH

Of all experimental parameters affecting basic dyes sorbed on PA-modified rice straw, the influences of initial pH were investigated first. The initial pH of dye solutions was researched over a range from 2 to 11. But for BR5, the experiments were only conducted from pH 2 to 5 for avoiding dye precipitation and color change. As elucidated in Fig. 1, for BB9 and BR5, the dye removal ratios were minimum at the initial pH 2. The percentages of dyes sorbed increased as the initial pH was increased from pH 2 to 4. Beyond pH 4, the maximum dye removal ratios were reached and the percentages of dyes sorbed kept basically unchangeable. For this reason, the natural pH values of dye solutions were selected for the other experiments.

3.2. Effect of sorbent dose

The effects of sorbent dose on the removal ratios of dyes are shown in Fig. 2. Along with the increase of sorbent dosage from 0.1 to 1.5 g/l, the percentages of dye sorbed increased from 10.87 to 98.39% and from 7.21 to 97.97% in BB9 and BR5, respectively. Above 1.5 g/l of sorbent dose, the sorption equilibriums of dyes were reached and the removal ratios of dyes held almost no variety. So, the sorbent dosage of 2.0 g/l was chosen for subsequent experiments.

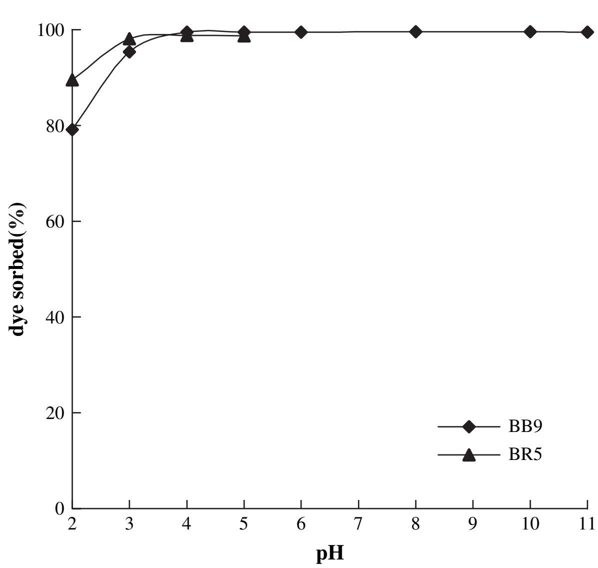


Fig. 1. Influence of initial pH on sorption of BB9 and BR5 by PA-modified rice straw (dye concentration: 250 mg/l; sorbent dose: 2 g/l; contact time: 6 h).

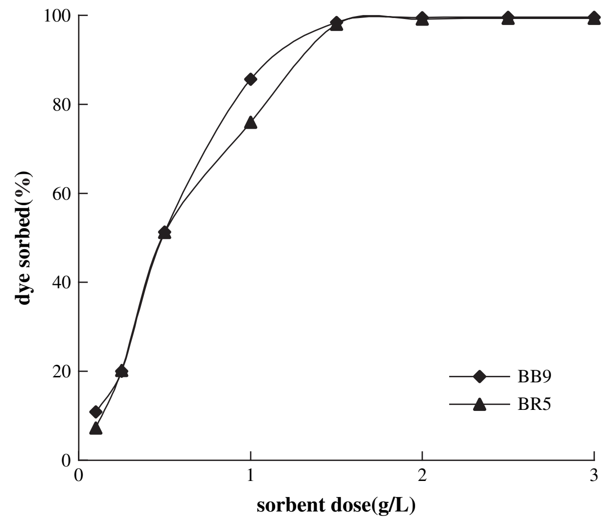


Fig. 2. Effect of sorbent dose on sorption of BB9 and BR5 by PA-modified rice straw (dye concentration: 250 mg/l; contact time: 6 h; pH: natural).

3.3. Influence of initial dye concentration

The influences of dye concentration on sorption percentages of dyes were estimated. As shown in Fig. 3, when the dye concentration was increased from 50 to 350 mg/l, the percentages of dyes sorbed were held above 98 and 96% for BB9 and BR5, respectively. But the higher dye concentrations would obviously decrease the removal ratios of dyes.

With the data in Fig. 3, Langmuir equation was employed to study the sorption isotherms of BB9 and BR5. The Langmuir equation is based on the assumption that maximum sorption corresponds to saturated monolayer of sorbate molecule on the sorbent surface, that the energy of sorption is constant and that there is no transmigration of sorbate in the plane of the surface. Langmuir isotherm was obtained by agitating the sorbent of fixed dose and the dye solutions of different concentration for a constant time greater than the sorption equilibrium time.

The non-linear Langmuir equation was expressed as follows:

$$q_e = aQ_mC_e/1 + aC_e$$

Above equation can be linearized in following reciprocal form:

$$C_e/q_e = 1/(aQ_m) + C_e/Q_m$$

where C_e (mg/l) is the concentration of the dye solution at equilibrium, q_e (mg/g) is the amount of dye sorbed at equilibrium, Q_m (mg/g) is the maximum sorption capacity and represents a practical limiting sorption capacity when the sorbent surface is fully covered with monolayer sorbate molecules and a is Langmuir constant. The Q_m and a values were calculated from the slopes ($1/Q_m$) and intercepts ($1/aQ_m$) of linear plots of C_e/q_e versus C_e.

The Langmuir sorption isotherms of BB9 and BR5 sorbed on PA-modified rice straw are presented in Fig. 4. The values

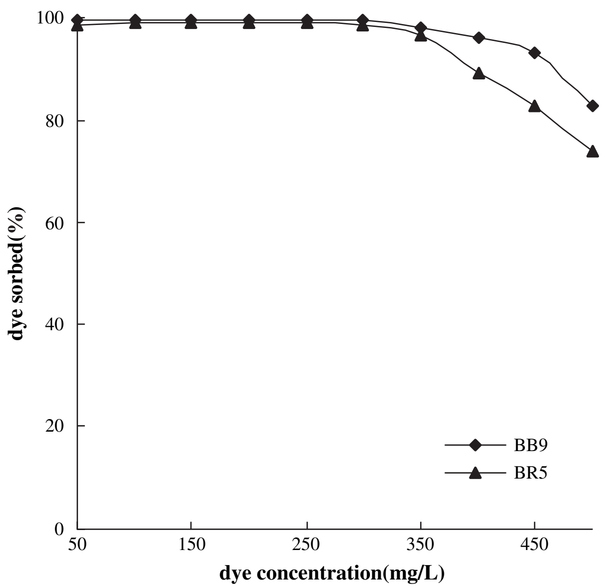


Fig. 3. Influence of dye concentration on sorption of BB9 and BR5 by PA-modified rice straw (sorbent dose: 2 g/l; contact time: 6 h; pH: natural).

of parameters, correlation coefficients and probability factors of the Langmuir equations are given in Table 1. The experimental results indicated that the sorption isotherms followed the Langmuir model. The maximum sorption capacity (Q_m) of PA-modified rice straw for BB9 and BR5 was 208.33 and 188.68 mg/g, respectively.

3.4. Effect of ion strength

The effects of ion strength on BB9 and BR5 sorbed on PA-modified rice straw were tested by the addition of sodium chloride to the dye solutions. The concentration of NaCl used ranged from 0 to 0.5 M. As seen in Fig. 5, increasing the ion strength of solution caused sharp decrease in sorption percentages of BB9. This could be attributed to the competition of BB9 cation and Na^+ ion for the sorption sites. But the effect of ion strength on sorption of BR5 was not remarkable.

Table 1
The values of parameters, correlation coefficients and probability factors of Langmuir equations

Dye	Langmuir			
	Q_m (mg/g)	a	R^2	p
BB9	208.33	0.9796	0.9998	<0.001
BR5	188.68	0.4649	0.9994	<0.001

3.5. Sorption kinetics

Fig. 6 illustrates the sorption kinetics of BB9 and BR5 sorbed on PA-modified rice straw. The removal rates of dyes were very rapid during the initial stages of the sorption processes. After a very rapid sorption, dye uptake rates slowly declined with lapse of time and reached equilibrium values at about 2 h and 4 h for BB9 and BR5, respectively. The three phases of dye sorption could be attributed to boundary layer sorption, intraparticle diffusion and sorption equilibrium, respectively.

The kinetic data of the first 80 min in Fig. 6 were treated with the following Lagergren's pseudo-first-order rate equation:

$$\lg(q_e - q_t) = \lg q_e - k_{ad}t/2.303$$

where q_e and q_t (mg/g) refer to the amount of dye sorbed at equilibrium and time t (min), respectively, and k_{ad} is the rate

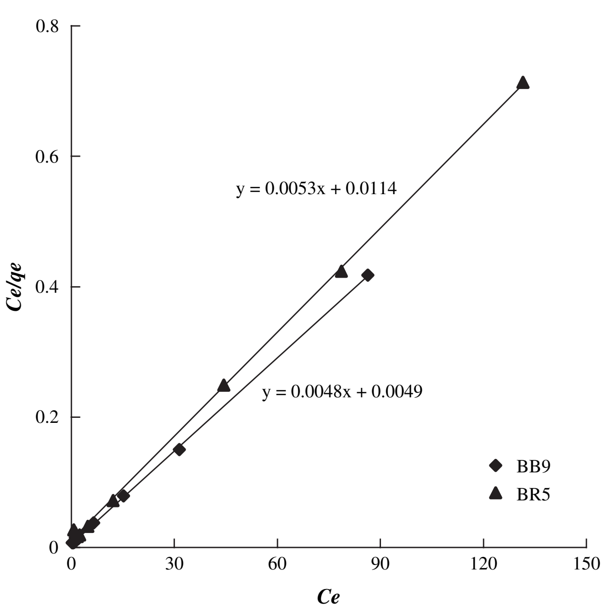


Fig. 4. Langmuir sorption isotherms of BB9 and BR5 by PA-modified rice straw.

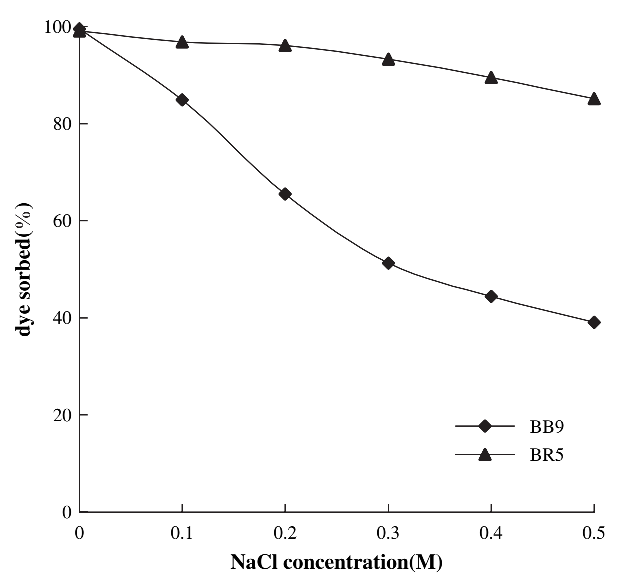


Fig. 5. Effect of ion strength on sorption of BB9 and BR5 by PA-modified rice straw (dye concentration: 250 mg/l; sorbent dose: 2 g/l; contact time: 6 h; pH: natural).

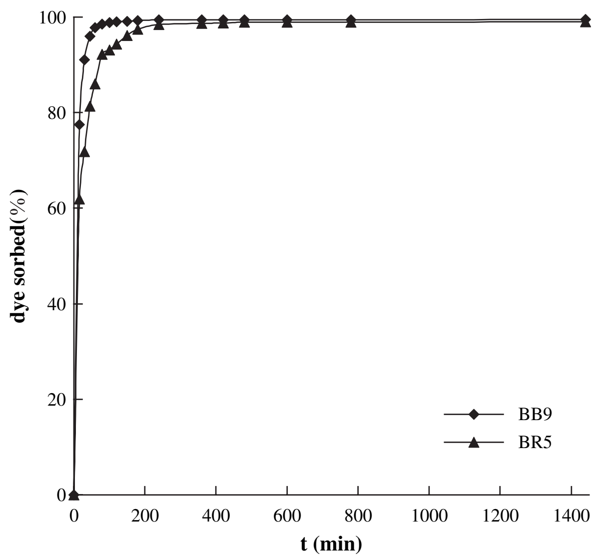


Fig. 6. Sorption kinetics of BB9 and BR5 by PA-modified rice straw (dye concentration: 250 mg/l; sorbent dose: 2 g/l; pH: natural).

constant. The rate constants k_{ad} could be calculated from the slopes of the linear plots of $\lg(q_e - q_t)$ versus t. The Lagergren plots of BB9 and BR5 sorption are shown in Fig. 7. The high values of correlation coefficients showed that the data conformed well to the pseudo-first-order rate kinetic model.

3.6. Total phosphorus content and basic dye removal capacity

The total phosphorus content and basic dye removal capacity of PA-modified rice straw are presented in Table 2. The data showed correlativity between phosphorus content and dye removal capacity. Deducting the phosphorus content of raw rice straw from the total phosphorus, the phosphorus content of PA-modified rice straw was basically in agreement with its basic dye removal capacity.

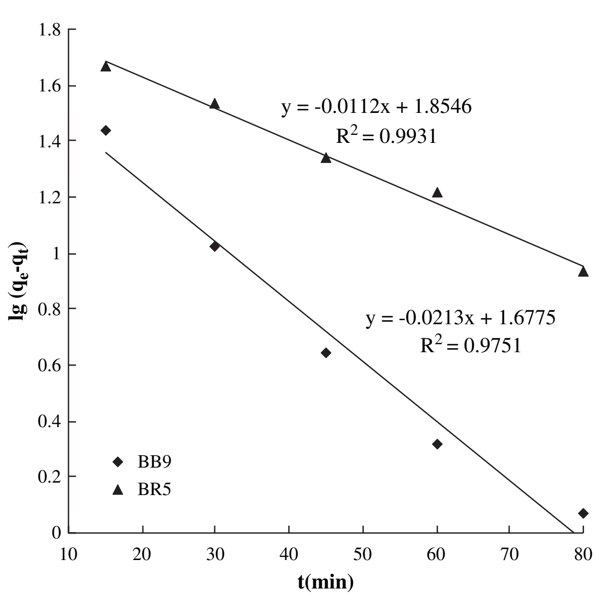


Fig. 7. Lagergren plots for sorption of BB9 and BR5 by PA-modified rice straw.

Table 2
The total phosphorus content and basic dye removal capacity of PA-modified rice straw

Sorbent	Total phosphorus (mM/g)	BB9 sorbed (mM/g)	BR5 sorbed (mM/g)
Raw rice straw	0.062	No datum	No datum
PA-modified rice straw	0.683	0.557	0.653

4. Conclusions

This study confirmed that PA-modified rice straw was an excellent sorbent for removal of basic dyes from aqueous solution. The optimal pH for favorable sorption was 4 and above. The 1.5 g/l or more sorbent could almost completely remove BB9 and BR5 from 250 mg/l of dye solution. The ratios of BB9 and BR5 sorbed kept above 96% over a range from 50 to 350 mg/l of dye concentration when 2.0 g/l of sorbent was used. Increase in ion strength of solution induced decline of BB9 and BR5 sorption. The isothermal data fitted the Langmuir model. The sorption capacities for BB9 and BR5 were 208.33 and 188.68 mg/g, respectively. The sorption processes followed the pseudo-first-order rate kinetics.

Acknowledgments

The first author was grateful for the financial support by the Key Laboratory of Bioresource Protection and Utilization of Anhui Province and by the Key Laboratory of Biotic Environment and Ecological Safety in Anhui Province.

References

[1] Nigam P, Armour G, Banat IM, Singh D, Marchant R. Physical removal of textile dyes from effluents and solid-state fermentation of dye-adsorbed agricultural residues. Bioresour Technol 2000;72:219–26.
[2] McKay G, Otterburn MS, Aga DA. Fullers earth and fired clay as adsorbent for dye stuffs, equilibrium and rate constants. Water Air Soil Pollut 1985;24:307–22.
[3] Gregory AR, Elliot S, Kluge P. Ames testing of direct black 3B parallel carcinogenicity. J Appl Toxicol 1991;1:308–13.
[4] Chinwetkitvanich S, Tuntoolvest M, Panswad T. Anaerobic decolorization of reactive dyebath effluents by a two-stage UASB system with tapioca as a co-substrate. Water Res 2000;34:2223–32.
[5] Seshadri S, Bishop PL, Agha AM. Anaerobic/aerobic treatment of selected azo dyes in wastewater. Waste Manag 1994;14:127–37.
[6] Panswed J, Wongchaisuwan S. Mechanism of dye wastewater color removal by magnesium carbonate-hydrated basic. Water Sci Technol 1986;18:139–44.
[7] Malik PK, Saha SK. Oxidation of direct dyes with hydrogen peroxide using ferrous ion as catalyst. Sep Purif Technol 2003;31:241–50.
[8] Koch M, Yediler A, Lienert D, Insel G, Kettrup A. Ozonation of hydrolyzed azo dye reactive yellow 84 (CI). Chemosphere 2002;46:109–13.
[9] Ciardelli G, Corsi L, Marucci M. Membrane separation for wastewater reuse in the textile industry. Resour Conserv Recycl 2000;31:189–97.
[10] Venkata RB, Sastray CA. Removal of dyes from water and wastewater by adsorption. Ind J Environ Prot 1987;7:363–76.

[11] Marshall WE, Champagne ET, Evans WJ. Use of rice milling by-products (hulls and bran) to remove metal ions from aqueous solution. J Environ Sci Health A 1993;28:1977−92.

[12] Marshall WE, Johns MM. Agricultural by-products as metal adsorbents: sorption properties and resistance to mechanical abrasion. J Chem Technol Biotechnol 1996;66:192−8.

[13] Namasivayam C, Muniasamy N, Gayatri K, Rani M, Ranganathan K. Removal of dyes from aqueous solutions by cellulosic waste orange peel. Bioresour Technol 1996;57:37−43.

[14] Namasivayam C, Prabha D, Kumutha M. Removal of direct red and acid brilliant blue by adsorption on to banana pith. Bioresour Technol 1998;64:77−9.

[15] Johnson PD, Watson MA, Brown J, Jefcoat IA. Peanut hull pellets as a single use sorbent for the capture of Cu (II) from wastewater. Waste Manag 2002;22:471−80.

[16] Robinson T, Chandran B, Nigam P. Removal of dyes from a synthetic textile dye effluent by biosorption on apple pomace and wheat straw. Water Res 2002;36:2824−30.

[17] Gong RM, Ding Y, Li M, Yang C, Liu HJ, Sun YZ. Utilization of powdered peanut hull as biosorbent for removal of anionic dyes from aqueous solution. Dyes Pigments 2005;64:187−92.

[18] Gong RM, Li M, Yang C, Sun YZ, Chen J. Removal of cationic dyes from aqueous solution by adsorption on peanut hull. J Hazard Mater 2005;121:247−50.

[19] Randall JM, Hautala E, McDonald G. Binding of heavy metal ions by formaldehyde polymerized peanut skins. J Appl Polym Sci 1978;22:379−87.

[20] Okieimen FE, Okundaye JN. Removal of cadmium and copper ions from aqueous solutions with thiolated corn maize cob meal. Biol Waste 1989;30:225−30.

[21] Laszlo JA, Dintzis FR. Crop residues as ion-exchange materials. Treatment of soybean hull and sugar beet fiber (pulp) with epichlorohydrin to improve cation-exchange capacity and physical stability. J Appl Polym Sci 1994;52:531−8.

[22] Wartelle LH, Marshall WE. Citric acid modified agricultural by-products as copper ion adsorbents. Adv Environ Res 2000;4:1−7.

[23] Hills DI, Roberts DW. Anaerobic digestion of dairy manure and field crop residues. Agric Waste 1981;3:179−89.

[24] Ghimire KN, Inoue K, Yamaguchi H, Makino K, Miyajima T. Adsorptive separation of arsenate and arsenite anions from aqueous medium by using orange waste. Water Res 2003;37:4945−53.