

A Novel Method in Utilization of Bokbunja Seed Wastes From Wineries in Liquid-Phase Sequestration of Reactive Blue 4

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Received 12 June 2008;

Revised 15 Sep. 2008;

Accepted 25 Sep. 2008

ABSTRACT: Bokbunja seed wastes from a wine manufacturing industry were used to prepare carbon for the purpose of using it as an adsorbent for the removal of Reactive Blue 4 from aqueous solutions. A part of prepared carbon was treated with *n*-hexane to remove the seed oil present in large amounts in Bokbunja seeds. It was found that the hexane treated carbon was more efficient in removing the dye from aqueous solutions. Optimization of process parameters showed that pH 2 and contact time of 120 min was favorable for maximum adsorption. Langmuir and Khan isotherm models were applied to comprehend the adsorption process. Kinetic data showed that pseudo-first order model was a better fit than the pseudo-second order model. Alkaline pH favored desorption. Among the various desorption medium tested, acetone and ethanol showed promising results thus enabling the reuse of the carbon for next adsorption cycle. The study justifies the efforts to minimize the wastes by firstly using a winery waste as adsorbent and later reusing the same for the next cycle of adsorption in addition to recycling the desorption medium while simultaneously recovering the adsorbed dyes.

Key words: Bokbunja seeds, Carbon, Adsorption, Reactive Blue, Isotherm, Kinetics

INTRODUCTION

The textile dyeing units release large quantities of dyes in their effluents (Nabi Bidhendi *et al.*, 2007). Over 70,000 tons of approximately 10,000 types of dyes and pigments are produced annually world wide, of which, about 20–30% are wasted in industrial effluents during the textile dyeing and finishing processes (Cooper, 1993). These dyes not only affect the aesthetic value of the receiving water body but also pose a major problem due to their resistance to chemical and biological degradation (Fu and Viraraghavan, 2002a). Many reactive azo dyes, constituting the largest dye groups decompose to potential carcinogenic aromatic amines under anaerobic conditions (Lazearidis *et al.*, 2003; Netpradit *et al.*, 2003). Existing conventional technologies have suffered several drawbacks due to their high costs and low regeneration. Adsorption has been found to be superior to other techniques for treating

wastewater: it is low-cost, highly efficient, simple, easy to perform and insensitive to toxic substances (Wu, 2007; Hassani *et al.*, 2008). Despite its generous use in water and wastewater industries, activated carbon remains an expensive material. This has led to search for low-cost adsorbent materials with potential to replace commercial activated carbons. Some agricultural wastes that have been converted to activated carbon for use in dye adsorption are olive kernels (Zabaniotou *et al.*, 2008), *Euphorbia rigida* (Gercel *et al.*, 2007), bamboo shoot (Hameed *et al.*, 2008) and jute fiber (Senthilkumaar *et al.*, 2005) for methylene blue removal, coconut flower for reactive red adsorption (Senthilkumaar, *et al.*, 2006), bamboo dust, coconut shell, groundnut shell, rice husk and straw for removal of Congo red and silk cotton hull for reactive blue removal (Thangamani *et al.*, 2007). Bokbunja or Korean wild raspberry (*Rubus coreanus* Miq.) is a

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deciduous broadleaf shrub in the family Rosaceae. It is mainly used to produce traditional wine by fermenting and maturing the fully ripened fruits harvested in June and July. The bokbunja harvest quantity rose from about 1510 tons in 2001 to 2733 tons in 2005 which shows that the industry has grown to a great extent due to the popularity of bokbunja wines (Ku and Mun, 2007). On the other hand, the wine industries are facing the problem of disposing large quantities of hard seeds of bokbunja left behind after processing the berries for wine production. The seed wastes are large enough to cause serious problems in these industries. A search for utilization of these seed wastes to minimize the waste is in wanting. In our study, studied the used of waste bokbuja seeds obtained from wine industry for the adsorption of Reactive blue dye from wastewaters. Reactive Blue 4 dye (RB) is an anthraquinone-based chlorotriazine dye very important in dyeing of cellulosic fabrics (Carneriro *et al.*, 2003). The effect of pH, contact time and initial concentration on dye adsorption was explored. The kinetic data and equilibrium data on batch adsorption studies were carried out to understand the adsorption process. To investigate the mechanism of Reactive Blue dye adsorption, characteristic adsorption constants were determined using pseudo first order and pseudo second order and compared.

MATERIALS & METHODS

The Bokbunja waste seeds discarded from wine processing were provided by Go-In-Dol Bokbunja Wine Company, Gochang, Korea. The seeds were washed with water many times to remove fibrous substances and pigments and dried in a convection oven at 60 °C for 24 h. The dried seeds were boiled in 0.1 M H₂SO₄ for 1 h to remove the remaining fibers adhering on the surface as they will increase the ash content if carbon is produced directly. The seeds were then washed with distilled water thoroughly until the pH of the spent solution was near neutral range (6.8-7.2) and dried in a convection oven at 60 °C for 24 h. Carbon was prepared by mixing one part of dried seeds with one part of concentrated H₂SO₄ (w/v) and maintaining at room temperature (30±2 °C) over night. The carbonized material was then washed with distilled water to remove free acid and soaked in 2% NaHCO₃ overnight to

remove any residual acid from the pores of the carbon. The material was further washed with distilled water until the pH of the adsorbent reached slightly above 7.0. Then, it was dried in a hot air oven at 120 °C for 6 h. The dried material was ground and sieved to a particle size of 125–250µm. This carbon was used for adsorptions studies as such. Bokbunja seeds are known to have high oil content (Ku and Mun, 2007). Therefore, a part of prepared carbon was treated with *n*-hexane to remove the remaining seed oil. The carbon was washed several times with *n*-hexane and dried in a hot air oven at 60 °C. The morphologies of the raw material and carbons prepared were examined by a scanning electron microscope (JEOL JSM-5410LV) under vacuum combined with energy dispersive X-ray spectroscopy (EDX). X-ray diffraction (XRD) patterns for the sorbents were obtained using a (D-Max-3A, Rigaku XRD) diffractometer in the 2θ range from 10° to 80° with Cu Kα radiation. All the chemicals used were of analytical reagent grade procured from Sigma-Aldrich, South Korea. All the solutions were prepared in double distilled water.

From here on the *n*-hexane untreated carbon is referred as HUTC and *n*-hexane treated carbon as HTC in the text. Reactive blue 4 (RB) was procured from Sigma-Aldrich, South Korea. The two and three dimensional dye structure is given in (Fig. 1). along with the distance between the atoms, which was calculated using Chemscketch software (ACDLabs, version 5.0). Molecular Formula: C₂₃H₁₄Cl₂N₆O₈S₂, Molecular Weight: 637.43, CAS Number: 13324-20-4; λ_{max} 595 nm. Standard solutions containing 10 - 80 mg/L of the dye was prepared by diluting a stock solution of 1000 mg/L of RB.

Batch adsorption studies were carried out by agitating 100 mg of adsorbent with 50 mL of dye solution of different initial concentrations (10, 20, 30, 40, 50, 60, 70 and 80 mg/L) at pH 2, 150 rpm, at 30±2 °C temperature in a thermostated rotary shaker. The flasks were withdrawn at predetermined time intervals. The adsorbent and adsorbate were separated by centrifugation at 3000 rpm for 20 min. The remaining adsorbate concentration in the supernatant was determined using a UV-VIS spectrophotometer (Shimadzu, UV-1601) at 595 nm from which the amount of dye adsorbed by the adsorbent (*q*, mg/g) was

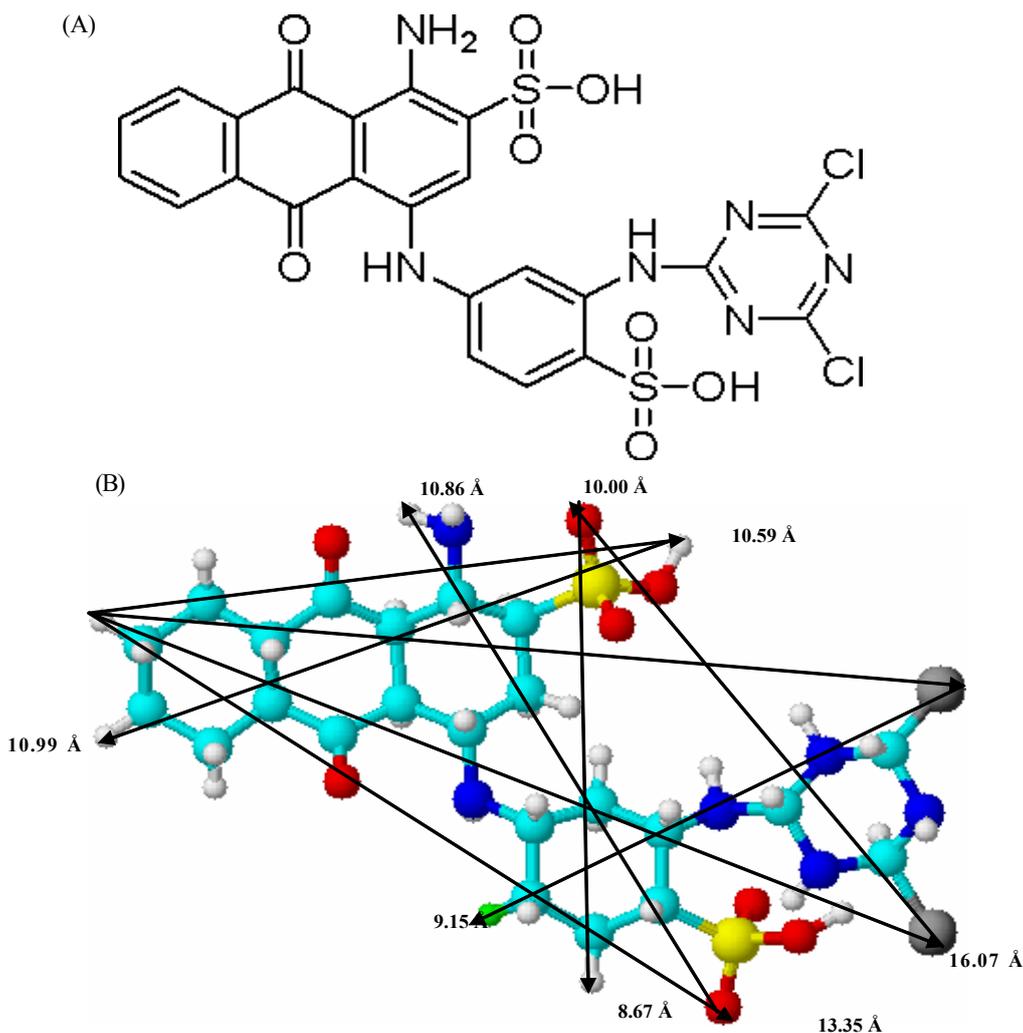


Fig. 1. Two (A) and three (B) dimensional structure of Reactive Blue R

calculated. The effect of pH on adsorption process was carried by varying the pH of 50 mL of 50 mg/L adsorbate solution between 2.0 to 10.0 using dilute HCl and NaOH solutions keeping the other experimental parameters same as described earlier. The effect of temperature on adsorption of RB by HUTC and HTC were also evaluated at 20 to 55 °C at pH 2 for 6 h with 50 mg/L adsorbate solution and 100 mg of adsorbent. Control experiments were carried out for the adsorption of RB in absence of carbon to ensure if the dye was adsorbed by container walls. However, it was found that the walls of the container did not take up RB.

Desorption studies were carried out with adsorbate-laden adsorbent obtained from a batch

process, in which the adsorbate solutions (50 mg/L of RB) were treated for the optimum contact time. The dye-laden carbon was washed gently with distilled water to remove unadsorbed RB. Several such samples were prepared. Then the spent adsorbent was agitated at 200 rpm for 5 h with 50 mL of distilled water, adjusted to different pH values (2-10). The desorbed RB was estimated spectrophotometrically as mentioned earlier. Similarly desorption studies were carried out in 50 mL of 1 N NaOH solution, 70% ethanol, 70% acetone and distilled water separately. The flasks were agitated at 200 rpm for equilibrium time. All the experiments were carried out in duplicate and the mean values are presented. The error obtained was $\pm 4\%$. The experimental adsorption kinetic data were modeled

using pseudo-first- and pseudo-second-order kinetics. The non-linear form of pseudo-first- and pseudo-second-order models are shown below as Eqs. (1) and (2), respectively (Ku *et al.*, 2007).

$$Q_t = Q_e (1 - \exp(-k_1 t)) \quad (1)$$

$$Q_t = \frac{Q_e^2 k t}{1 + Q_e k t} \quad (2)$$

where Q_e is the amount of RB sorbed at equilibrium (mg/g); Q_t is the amount of RB sorbed at time t (mg/g); k_1 is the first order equilibrium rate constant (1/min) and k_2 is the second order equilibrium rate constant (g/mg min). A two-parameter and a three-parameter isotherm model (Langmuir and Khan) were used to describe the non-linear equilibrium relationship between the solute sorbed onto the sorbent (Q) and that left in solution (C_f). The model equations can be represented as, Two-parameter model:

$$\text{Langmuir model: } Q = \frac{Q_{\max} b C_f}{1 + b C_f} \quad (3)$$

Three-parameter model:

$$\text{Khan model: } Q = \frac{Q_{\max} b_K C_f}{(1 + b_K C_f)^{a_K}} \quad (4)$$

where Q_{\max} is the maximum RB uptake (mg/g), b the Langmuir equilibrium constant (l/mg), b_K is the Khan model constant and a_K the Khan model exponent. All isotherm and kinetic model parameters were evaluated using non-linear regression employing the Sigma Plot (version 4.0, SPSS, USA) software (Sathishkumar *et al.*, 2007a). The average percentage error between the experimental and predicted values was calculated using:

$$\varepsilon (\%) = \frac{\sum_{i=1}^N (Q_{\text{exp},i} - Q_{\text{cal},i} / Q_{\text{exp},i})}{N} \times 100 \quad (4)$$

where Q_{exp} and Q_{cal} represent the experimental and calculated uptake values, respectively, and N the number of measurements. The residual root mean square error (RMSE) and the Chi-square test were also used to measure the goodness-of-fit. RMSE can be defined as:

$$RMSE = \sqrt{\frac{1}{m-2} \sum_{i=1}^m (Q_i - q_i)^2} \quad (6)$$

where Q_i is the observation from the batch experiment, q_i is the estimate from the isotherm for corresponding Q_i and m is the number of observations in the experimental isotherm. The smaller RMSE value indicates the better curve fitting. The Chi-square test can be defined as:

$$\chi^2 = \sum_{i=1}^m \frac{(Q_i - q_i)^2}{q_i} \quad (7)$$

If data from model are similar to the experimental data, χ^2 will be a small number (Ho *et al.*, 2005).

RESULTS & DISCUSSION

SEM images of the Bokbunja seed carbon before and after acid pretreatment are shown in (Fig.2). The SEM micrograph of the carbon before acid pretreatment shows rough pore-less surface with lot of pulp residues on the surface. After acid treatment, development of large serrated pores can be observed in (Fig 2B). This confirms the removal of fruit pulp and fibers by acid treatment. Removal of pulp and fibers will favor in production of high quality carbon with less ash content. High ash content is always known to reduce the adsorption capacity of carbon. The macro and meso-pores more or less appear to be uniform throughout the prepared carbon (Fig. 2C and 2D). The activation process of precursor material by adopting sulphuric acid treatment may cause corrosion of the surface of carbonaceous material and introduce micro-, macro- and meso-pores (Thangamani *et al.*, 2007). Characteristics of carbon prepared from Bokbunja seed are presented in Table 1. The measured BET surface area of HUTC and HTC were 1494 and 1889 m²/Kg, respectively and is comparable to various recently reported low cost adsorbents namely, coir pith carbon (1900 m²/Kg) (Namasivayam and Sureshkumar, 2008), and Avacado fruit peel carbon (750 m²/Kg) (Devi *et al.*, 2008). The average pore diameter of HUTC and HTC were 19.7 and 21.2 Å, respectively. From fig. 1 it is clear that the size of RB at any angle does not exceed the average pore diameter of both HUTC and HTC. Thus the mobility of the dye molecule into the pores will be easier without any hindrance.

The moisture content of HUTC and HTC were found to be 3.87 and 4.01%. It was then observed from the literature that if the moisture content of the adsorbent is more, it will dilute the action of carbon and it necessitates utilizing some extra load of carbon (Thangamani *et al.*, 2007). The phenol adsorption capacity of HUTC and HTC were 9.56 and 9.87 mg/g respectively, which indicates that the carbon prepared by the acid activation method had good adsorption capacity and it could be used for adsorption of organic dyes. EDX analysis showed 59% of carbon and 39% of oxygen (Table 1). High percentage of sulfur may be due to sulphuric acid treatment during preparation of carbon. X-ray Diffraction studies of prepared carbon revealed the amorphous nature of it.

Table 1. Characteristics of Bokbunja carbon

Parameters	HUTC	HTC
pH (1% Solution)	6.57	6.85
Moisture content (%)	3.87	4.01
Ash content (%)	1.25	1.06
Phenol adsorption capacity (mg/g)	9.56	9.87
BET Surface area (m ² /Kg)	1494	1889
Single point Surface area (m ² /Kg)	1162	1485
Langmuir Surface area (m ² /Kg)	2085	2757
Total pore volume (cm ³ /g)	0.217	0.341
Average pore dia (Å)	20	34
Carbon (%)	59.2	59.7
Oxygen (%)	38.6	37.8
Sodium (%)	0.33	0.39
Potassium (%)	0.13	0.21
Sulfur (%)	1.78	1.91

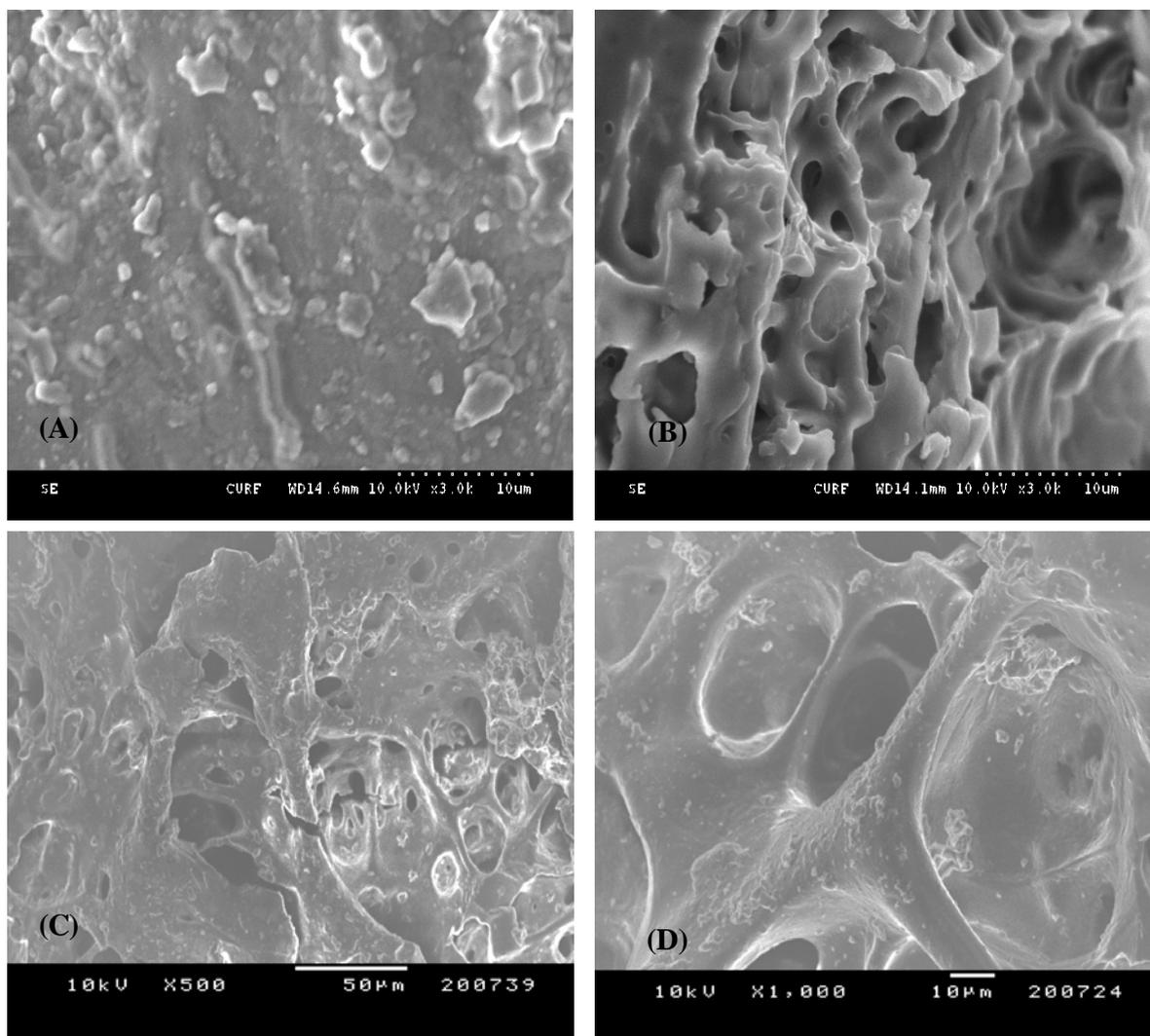


Fig. 2. SEM Micrographs of Bokbunja seed: (A) Natural seed surface; (B) Acid treated seed surface; (C) HUTC; (D) HTC

Textile dyes have different ionization potentials at different pH due to the presence of various functional groups. The chemical interaction between the dye molecules and the adsorbents depend on the chemical composition of the adsorbent and the dye. At different pH the ionic nature of the dye varies as does the electric charge on the adsorbent surface which dictates their interaction (Maurya *et al.*, 2006). The effect of pH on RB adsorption by HUTC carbon is given in (Fig. 3). Adsorption of RB on both carbons increased with decrease in pH with maximum dye adsorption being at pH 2. Reactive blue 4 molecules have 2 sulphonate groups and one primary amine group. These groups assume negative and positive charges respectively under different pH conditions. Similarly the adsorbent also will have cations like Na and K on its surface which also will act as binding sites of RB. Lowering the solution pH increases the number of positive groups on the surface of the adsorbent thereby enhancing the uptake of negatively charged dye molecules. At low pH conditions the number of binding sites on the carbon increases concurrently increasing adsorption. Activated carbon normally contains varying amounts of water molecules especially those which either exist as surface hydroxyl groups or adsorbed water. At acidic pH, an increasing concentration of the H^+ ion in dye solution, the surface OH^- ions would get neutralized by protonation, which facilitates the diffusion of dye molecules in the vicinity of the adsorbent. Consequently the positive charge density would be located more on the dye molecule at pH 2, and this accounts for the higher dye uptake on the negatively charged surface. Thus it seems likely that the negative charge density on the surface will increase and will be associated with H^+ or Na^+ or K^+ ions according to the pH of the solution. These positively charged ions in the presence of dye solution could then be exchanged with dye cations (Kavitha and Namasivayam, 2007). Bayramoglu *et al.* (2006) reported maximum adsorption of RB at pH 3 by fungal biomass and Senthilkumaar *et al.* (2006) reported similar results with reactive red using activated carbon.

The effect of initial dye concentration on adsorption of RB onto HUTC and HTC was investigated in the range of 10–60 mg/L of the initial dye concentrations with adsorbent dose of

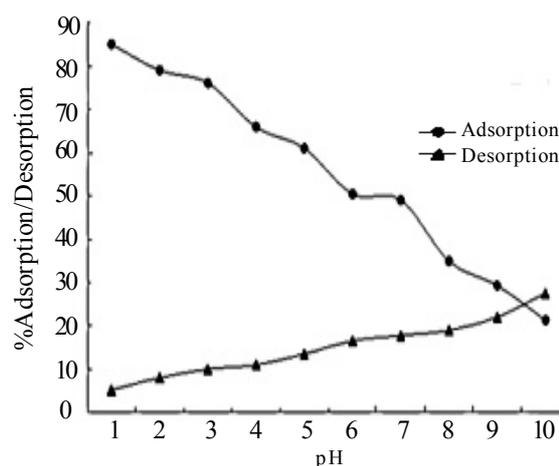


Fig. 3. Effect of pH on adsorption and desorption of RB by HUTC: Initial RB concentration 50 mg/L; Adsorbent dosage 100 mg/50 mL; Temperature 30 °C

100 mg, at pH 2 and 30°C. A rapid increase in per cent adsorption of RB was observed initially which gradually reduced with increase in time and finally ended with zero removal for both HUTC and HTC. A decreasing trend in per cent adsorption with increase in initial dye concentration is distinct from (Fig. 4). The amount of dye removal at equilibrium increased with increase in the dye concentration; hence dye removal was concentration dependant. Irrespective of initial dye concentration it was observed that adsorption equilibrium was attained at 120 minutes in all concentrations and by both adsorbents. Strong chemical binding of the adsorbate with adsorbent requires a longer contact time for the attainment of equilibrium (Mall *et al.*, 2006). Dye sequestration was high during the first 40 minutes in all concentration ranges from 10 to 60 mg/L by both carbons. The amount of dye adsorbed (mg/g) increased with increases in agitation time and finally reached equilibrium. The equilibrium time for further studies was taken as 120 min for all dye concentrations. In this study, for an initial dye concentration of 10 mg/L, the maximum amount of dye adsorbed by HUTC and HTC at initial 50 min was with an average biosorption rate of 0.543 mg/g and 0.725 mg/g respectively. However the biosorption rate declined as it approached equilibrium with an average biosorption rate of 0.061 mg/g and 0.158 mg/g for HUTC and HTC respectively during the last 50 min. A similar trend was observed for the

remaining range of the initial dye concentrations (20 – 50 mg/L) studied. At very low concentrations the availability of active sites on the carbons are more, on the contrary with increase in dye concentrations, competition for the number of active sites available increases resulting in low adsorption percentage. The initial rapid phase may be due to the availability of a greater number of biosorption/vacant sites at start of the experiment resulting in an increased concentration gradient between adsorbate in solution and adsorbate in the adsorbent (Sathishkumar *et al.*, 2007b). Asfour *et al.* (1995) explained that this might be due to strong attractive forces between the dye molecules and the sorbent and fast diffusion into the intra-particle matrix to attain rapid equilibrium.

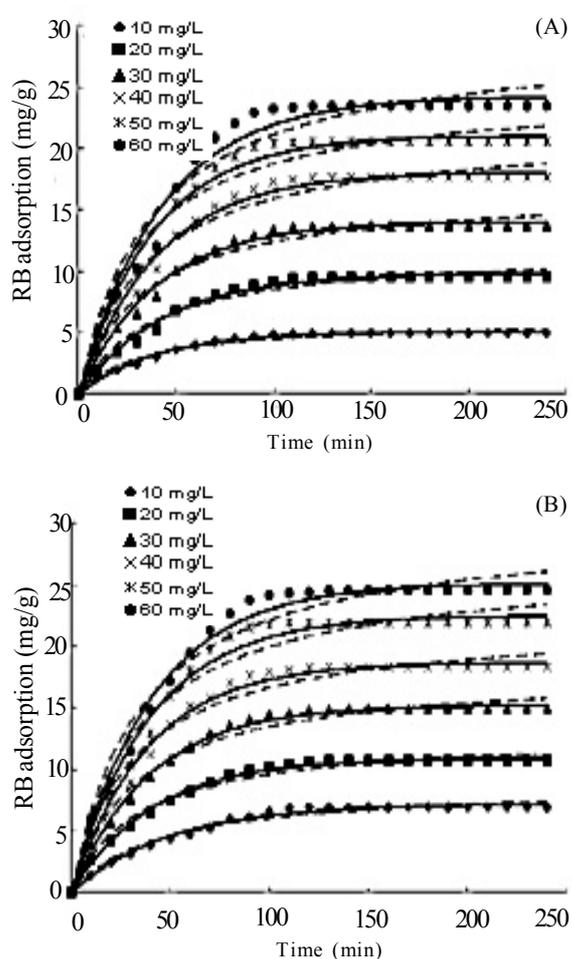


Fig. 4. Effect of contact time on adsorption of RB onto HUTC (A) and HTC (B): Adsorbent dosage 100 mg/50 mL; pH 7.0; Temperature 30 °C. Curves predicted by the First order rate expression (—) and the Pseudo-second order expression (-----)

Desorption studies help to elucidate the mechanism of biosorption and also help in the recovery of dye and adsorbent, which makes the treatment process more economical, since it is necessary to regenerate the spent biomass and dye. Desorption of RB was carried out at different pH from 2-10 for dye-laden HUTC and HTC. Results showed that for both carbons, the percentage desorption was less than percentage adsorption although the percent of dye desorbed increased as the pH was increased from 2 to 10 (Fig. 3). Probably chemisorptions were also involved in dye removal as extraction of dye from the adsorbent at different pH was difficult which indicates strong binding affinities between the dye molecules and the adsorbents. The desorbed dye could be only the physisorbed dye molecules on to the carbons by weak Vander waals force (Sathishkumar *et al.*, 2007a). Similar results have been reported by Namasivayam and Kavitha (2002), Binupriya *et al.* (2007) and Sathishkumar *et al.* (2007) for removal of dyes by coir pith carbon, *Trametes versicolor* and *Panus fulvus* respectively. From an industrial point of view, regeneration and reuse of the adsorbent is of prime importance as it reflects on the cost and labor of application. Therefore, desorption using various solvents such as water, ethanol (70%) and acetone (70%) and also a strong alkali (2 N NaOH) were attempted. Acetone, ethanol, NaOH and water showed 78.34, 56.38, 94.8 and 1.65% desorption, respectively (Fig. 5). The results prove that the adsorbents can be used for the next cycle of adsorption. Since the highly volatile industrial solvents (acetone/ethanol) proved to be good desorption medium, they can be recovered by distillation and the desorbed dyes also separated, making the process economical.

Adsorption isotherms are required to design adsorption systems hence considered important in adsorption studies. The most widely used two-parameter isotherm equation for modeling equilibrium is the Langmuir equation, based on the assumption that there is a finite number of binding sites which are homogeneously distributed over the adsorbent surface, these binding sites have the same affinity for adsorption of a single molecular layer and there is no interaction between adsorbed molecules (Langmuir, 1918). The adsorption capacity (Q_{max}) values were high in the

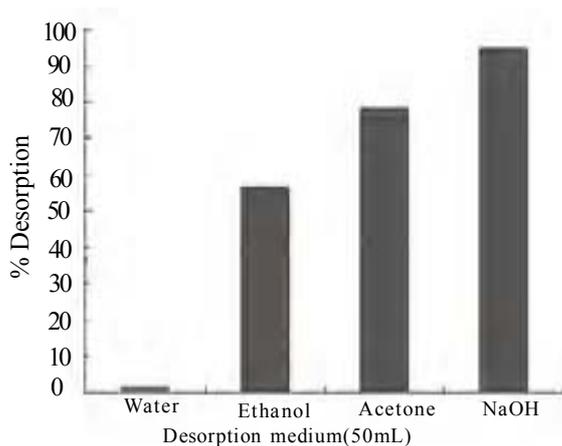


Fig. 5. Desorption of RB by HUTC in various medium: Adsorbent dosage 100 mg /50 mL; Temperature 30 °C

case of HTC carbon than HUTC carbon. The adsorption capacity of HUTC was 25.44 whereas that of HTC was 26.16 mg/g (Table 2). Both Q_{max} and b were slightly higher in the case of HTC than HUTC. This may be attributed to the less oil content in HTC which will facilitate the high possibility of active site interaction to the sorbate. High values of b are reflected in the steep initial slope of a sorption isotherm, indicating desirable high affinity. Thus, for good biosorbents in general, high Q_{max} and a steep initial isotherm slope (i.e. high b) are desirable. The three-parameter Khan isotherm model used to compare the fit of the present experimental data for HUTC and HTC did not show a good fit, comparatively (Fig. 6). The RMSE and chi-square values were also high for Khan isotherm model compared to Langmuir model, which shows the poor fit of the model to the present data (Table 2). Fu and Viraraghavan (2002b) where the adsorption capacities of live, autoclaved and alkali pretreated biomass of *Aspergillus Niger* to remove Congo red were 12.1, 13.47, and 11.17 mg/g, respectively. Commercial activated carbon, bagasse fly ash and coir pith carbon were known to remove 0.64, 11.89 and 6.72 mg/g of Congo red (Namasivayam and Kavitha, 2002; Mall *et al.*, 2005). Thangamani *et al.* (2007) reported 12.9 mg/g adsorption of Reactive blue-MR by carbonized silk cotton hull. Recently, carbonized sugarcane bagasse pith was reported to adsorb 3.48 mg/g of reactive orange (Amin, 2008). Compared to all the above said adsorbents for their adsorption efficacy towards

reactive dyes, HUTC and HTC prove to be a better candidate. For the amount of Bokbunja seed waste that is getting generated from the wineries presently in Korea, utilization of it for environmental technologies like adsorption will definitely be a better waste management strategy.

A first-order kinetic model was originally proposed by Lagergren and Svenska (1898) and a second-order model was put forward by Ho and McKay (1999). In the present study, we have used a non-linear form of first- and second-order kinetic model (Ku *et al.*, 2007). Although correlation coefficients for first order and second order plots were found to be 0.994 to 0.999 for both carbons, the theoretical q_e value was found to be in close agreement with experimental q_e in the case of Lagergren plots, suggesting that the model was

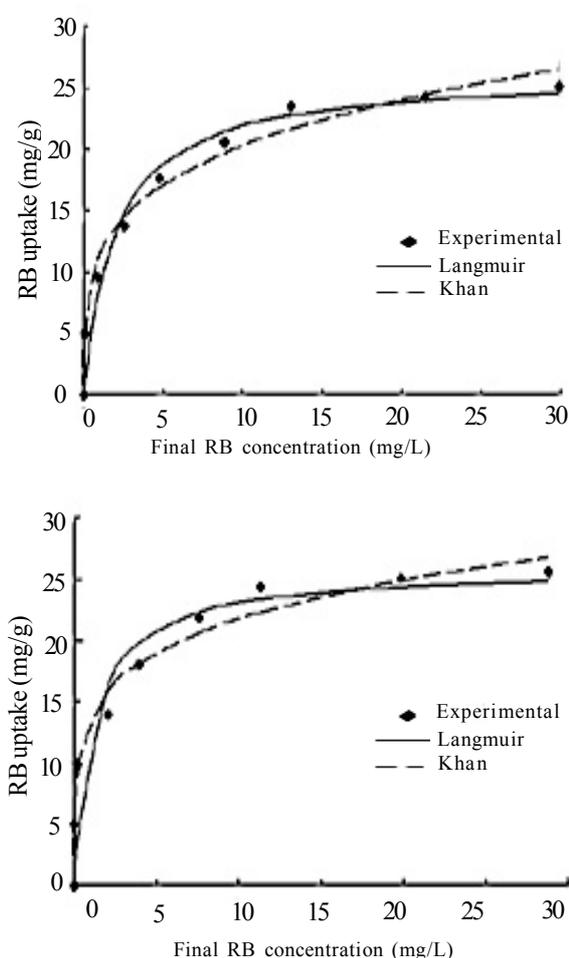


Fig. 6. Adsorption isotherms for adsorption of RB onto HUTC (A) and HTC (B): Adsorbent dosage 100 mg /50 mL; pH 7.0; Temperature 30 °C

Table 2. Isothermal parameters for the removal of RB by Bokbunja carbon

Isothermal models	Model parameters	HUTC	HTC
<i>Two parameter model</i>			
Langmuir	Q_{max}	25.44	26.16
	b_L	0.558	0.828
	R^2	0.994	0.988
	x^2	0.20	0.83
	$RMSE$	0.14	0.46
	ϵ (%)	1.11	1.70
<i>Three parameter model</i>			
Khan	Q_{max}	5.80	6.91
	b_K	28.04	36.16
	a_K	0.78	0.81
	R^2	0.992	0.976
	x^2	0.41	0.92
	$RMSE$	0.27	0.73
	ϵ (%)	1.55	1.58

suitable to fit the experimental kinetic data for the initial concentrations examined for HUTC and HTC. The parameters of the pseudo first- order model are summarized in Table 3. The pseudo-first-

order model assumes that the rate of change of solute uptake with time is directly proportional to the difference in saturation concentration and the amount of solid uptake with time. Sathishkumar et al. (2007a) also reported that adsorption rate kinetics for Procion blue H-B by *Panus fulvus* followed pseudo-first-order model. The pseudo-second-order model is based on the sorption capacity of the solid phase. Contrary to other well established models, it predicts the behavior over the entire range studied and it is in agreement with the chemisorptions mechanism being the rate controlling step (McKay et al., 1999). The q_e values obtained from the experiment and kinetics are listed in (Table 3), along with the other kinetic constants which show that the theoretical q_e value predicted by pseudo-second-order model did not agree with the experimental q_e value. It is therefore concluded that this adsorption system was not a second-order reaction at low dye concentration. Similar results were reported by Won et al. (2006) for the adsorption of reactive red 4 onto protonated coke waste.

The adsorption efficiency of HUTC and HTC was tested at temperatures ranging from 20 to 55 °C at pH 2 for 6 h with 50 mg/L adsorbate solution and 100 mg of adsorbent. The results showed that

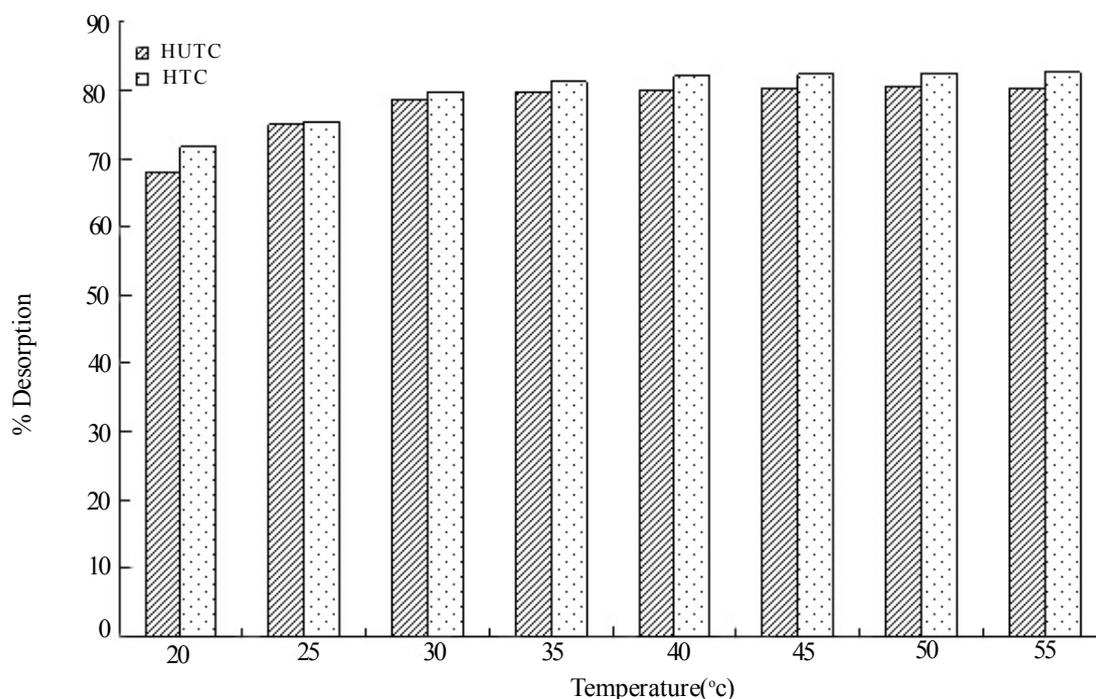


Fig. 7. Effect of temperature on adsorption of RB onto HUTC and HTC: Initial RB concentration 50 mg/L; Adsorbent dosage 100 mg/50 mL; pH 2.0

Table 3. Kinetic parameters for the removal of RB by Bokbunja carbon

Initial PR conc. (mg/L)	q_e (mg/g) (exp)	First order kinetic model						Second order kinetic model					
		k_1 (1/min) $\times 10^{-2}$	q_e (cal) (mg/g)	R^2	RMSE	χ^2	ε (%)	k_2 (g/mg/min) $\times 10^{-2}$	q_e (cal) (mg/g)	R^2	RMSE	χ^2	ε (%)
HUTC													
10	4.97	2.53	5.07	0.999	0.18	1.21	4.70	0.51	5.96	0.997	0.22	1.95	4.37
20	9.56	2.30	9.83	0.999	0.01	0.31	1.02	0.22	11.79	0.997	0.01	0.88	2.24
30	13.72	2.50	14.01	0.999	0.01	0.24	0.31	0.18	16.54	0.997	0.02	0.87	0.83
40	17.63	2.44	18.07	0.999	0.01	0.51	0.41	0.13	21.45	0.997	0.04	1.53	1.61
50	20.57	2.58	21.06	0.999	0.02	0.72	0.53	0.13	24.75	0.996	0.06	1.99	1.69
60	23.48	2.35	24.24	0.998	0.07	2.53	4.19	0.09	29.05	0.994	0.14	4.77	5.54
HTC													
10	6.95	2.04	7.20	0.999	0.20	1.00	2.33	0.25	8.80	0.997	0.30	1.41	2.03
20	10.7	2.45	10.92	0.999	0.01	0.22	0.23	0.23	12.91	0.998	0.01	0.73	1.41
30	14.92	2.53	15.21	0.999	0.01	0.07	1.13	0.17	17.91	0.998	0.01	0.57	0.02
40	18.29	2.6	18.67	0.999	0.01	0.41	0.11	0.14	21.92	0.997	0.03	1.37	1.27
50	21.95	2.53	22.53	0.999	0.02	0.64	0.25	0.11	26.63	0.996	0.05	1.85	0.05
60	24.53	2.45	25.16	0.999	0.06	2.18	3.25	0.10	29.84	0.996	0.13	4.28	4.55

increase in temperature increased RB removal. However, it was observed that there was notable increase in RB removal efficiency when the temperature was raised from 20 to 30 °C (Fig. 7). This indicates that adsorption is driven by endothermic process which results in enhanced rate of dye diffusion (Gercel *et al.*, 2007; Cicek *et al.*, 2007). Further increase in temperature had negligible effect on the adsorption process. The difference between the unit uptake between the minimum and maximum removal was only 6.1 mg/g for HUTC and 5.5 mg/g for HTC. From the results it is clear that the Bokbunja carbon is capable of performing at wider temperature ranges.

CONCLUSION

Bokbunja seeds, a waste from the Bokbunja wine making industry were used to prepare carbon and used as adsorbent for the removal of Reactive Blue from aqueous solutions. From the results we can conclude that removal of oil from the seed wastes enhances the dye adsorption capacity of Bokbunja carbon. High biosorption capacity was observed at lower pH. The adsorption kinetics followed pseudo-first order kinetic model. Acetone and ethanol were found to be good desorption medium enabling the reuse of the carbon for next adsorption cycle. The probability of reutilization of the highly volatile desorption medium is also very high. The study has considered minimizing the step by step production of wastes by primarily converting the winery waste as an effective dye adsorbent. It has explored the reuse of the adsorbent for the next cycle. However recycling of desorption medium while simultaneously recovering the desorbed dyes needs to be explored to make it a zero waste discharge system.

ACKNOWLEDGEMENTS

This research was partly supported by Chonbuk National University Post-Doctoral Research fund (2007) and partly by Research Center for Industrial Development of Biofood Materials in Chonbuk National University, Chonju, Korea. The center is designated as a Regional innovation Center appointed by the Ministry of Commerce, Industry and Energy (MOCIE), Jeollabuk-do Provincial Government and Chonbuk National University.

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