

## Removal of reactive dye using novel low cost activated carbon obtained from *Prunus × yedoensis* leaf by chemical activation

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The eco-friendly production of activated carbon from *Prunus × yedoensis* tree leaf (PYTL) for the removal of Remazol brilliant violet-5R reactive (RBV) dye has been studied for the first time. This carbon has been obtained by the chemical carbonization using concentrated H<sub>2</sub>SO<sub>4</sub> in a ratio of 2:1 (H<sub>2</sub>SO<sub>4</sub> : PYTL, v/w) followed by drying at 150°C for 24 hr. The RBV treated and untreated carbon is characterized using HR-FESEM, EDS, XRD, FTIR, and BET analysis. The PYTL carbon is found to be 100 mg/L, maximum removal of 10 ppm, in the time frame 60 min and the desorption 20 mg/L.

**Keywords:** Biomaterials, Carbon material, *Prunus × yedoensis*, Characterization, Adsorption, Remazol brilliant violet-5R.

Wastewater and water treatment is now becoming most crucial due to increasing industrial pollution with environmental concern, especially dyeing industry. Dyes, hazardous and toxic materials discharged through industrial effluents by way of adsorption are of great significance in connection with human health safety, aquatic life, food web and eco systems<sup>1,2</sup>. Earlier activated carbon obtained from fossil fuels<sup>3</sup>. However, these resources are now in short supply, and are mainly used to fulfill the nation need. Earlier several studies demonstrated that the

activated carbon have been produced from agricultural by-products like peat moss, sugar-cane pulp, coconut hulls, sheep-manure waste, groundnut shells and sawdust, jute fiber, and thiol cotton fiber<sup>4-6</sup> for removal of dye. In connection with this, we have prepared activated carbon from easily available substrate waste from *Prunus × yedoensis* tree leaf (PYTL) as raw materials.

The *Prunus × yedoensis* trees are generally one of the most popular and widely plantations in South Korea. There are several studies have been done using PYTL for the synthesis of platinum and palladium nanoparticles<sup>7,8</sup>. In this study, we investigated a novel activated carbon obtain by chemical carbonization *Prunus × yedoensis* leaf using H<sub>2</sub>SO<sub>4</sub> applied for the effective removal of Remazol Brilliant Violet-5R (RBV) from aqueous solution.

### Experimental Section

#### Preparation of *Prunus × yedoensis* leaves carbon (PYLC) absorbent

*Prunus × yedoensis* leaves were collected in and around Chonbuk National University, Iksan, South Korea, and washed thoroughly with nanopure water (conductivity 18 μΩ/m, TOC 3 ppb, Barnstead, Waltham, MA, USA). The collected leaves (100 g) were dried in sunlight and crushed using a mortar and pestle, and sieved to obtain a mean particle size of 500 μm. The powder was washed with deionized water to remove the leachable impurities. They leaves powder then mixed with concentrated H<sub>2</sub>SO<sub>4</sub> in a ratio of 2:1 (H<sub>2</sub>SO<sub>4</sub> : *Prunus × yedoensis* leaves, v/w) to obtain activated carbon through chemical carbonization by direct method and was kept at 150°C in hot air oven for 24 hr for drying.

Impregnation ratio

$$= \frac{\text{Weight of H}_2\text{SO}_4}{\text{Weight of dried } Prunus \times yedoensis \text{ leaves}}$$

After drying, the carbon was subject to continues washing with deionized water until supernatant pH was stable and finally it was treated with 2% NaHCO<sub>3</sub> (w/v) to remove residual acid from the absorbent. Then again the carbon was washed with deionized water several times and dried in a hot air oven at 105°C for 8 hr and sieved to get uniform carbon particles<sup>9,10</sup>.

### Preparation of dye stock

The stock solution was prepared for 1000 mg/L of RBV (industrial dye supplied by Sigma-Aldrich) by dissolving particular amount of dye in deionized water. Different concentration of dye solution was prepared from the stock solution and were stored in brown bottles to avoid photodegradation<sup>11</sup>. The absorbance measurement was carried out for RBV using UV-Vis spectrophotometer (UV – 1800, Shimadzu, Kyoto, Japan) at its absorbance maxima of 577 nm<sup>12</sup>. The properties of RBV dye are as shown in Table 1.

### Removal Efficiency of the obtain carbon and removal optimization

Preliminary studies were made with 25 mL of RBV aqueous solution (10 ppm) agitated with the adsorbent at 250 rpm and the removal was monitored for 1 h. On the observation of color removal the same was experimented with different doses of adsorbent (20, 40, 60, 80, 100 mg/L), varying dye concentrations (10, 20, 30, 40, 50 ppm), time frame (10, 20, 30, 40, 50, 60, 70, 80 min) and desorption experiment at (20, 40, 60, 80, 100 mg/L) along with necessary blanks and control samples at a constant pH-6.0 at ambient temperature.

### Characterization of PYLC

The dye treated and un treated PYLC surfaces structure, texture and elements were examined with a high resolution-field emission scanning electron microscopy (HR-FESEM, EDS,SU-8230, Hitachi, Japan). Crystal structure of dye treated and un treated PYLC were determined through X-ray diffraction (Rigaku X-ray diffract meter, Japan)in the 2θ-range from 20 to 80° with a step size of 0.02°. Fourier transform infrared (FTIR) spectra (Perkin-Elmer

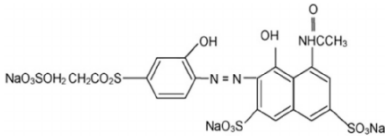
FTIR spectrophotometer, Norwalk, CT, USA) was used to analyze the functional group of dye treated and un treated PYLC in the diffuse reflectance mode at are solution of 4cm<sup>-1</sup> in KBr pellets. To determine the pore structure of dye treated and un treated PYLC obtained under preferable conditions, nitrogen adsorption–desorption isotherms were performed at –196°C using a surface area and porosity analyzer. Surface area ( $S_{BET}$ ) and micropore size were calculated with the Brunauer–Emmett–Teller (BET) method.

### Results and Discussion

Figure 1 shows the HR-FESEM images of adsorbents at various magnifications, it show that the active and high surface areaof the PYLC (dye untreated) is capable of readily adsorbing the dye molecules Fig. 1a-e. The image indicate that the leaf material swelled during preparation process due to the sulphuric acid activator.

From the image it was evident that the pores of activated carbon expanded in both quantity and

Table 1 — Properties of RBV dye

S. No	Dye name	Remazol brilliant violet-5R (RBV-5R)
1	Molecular formula	C <sub>20</sub> H <sub>16</sub> N <sub>3</sub> Na <sub>3</sub> O <sub>15</sub> S <sub>4</sub>
2	Molecular weight (g/mol)	735.58
3	CAS no.	12226-38-9
4	λ <sub>max</sub> (nm)	577
5	Chemical structure	

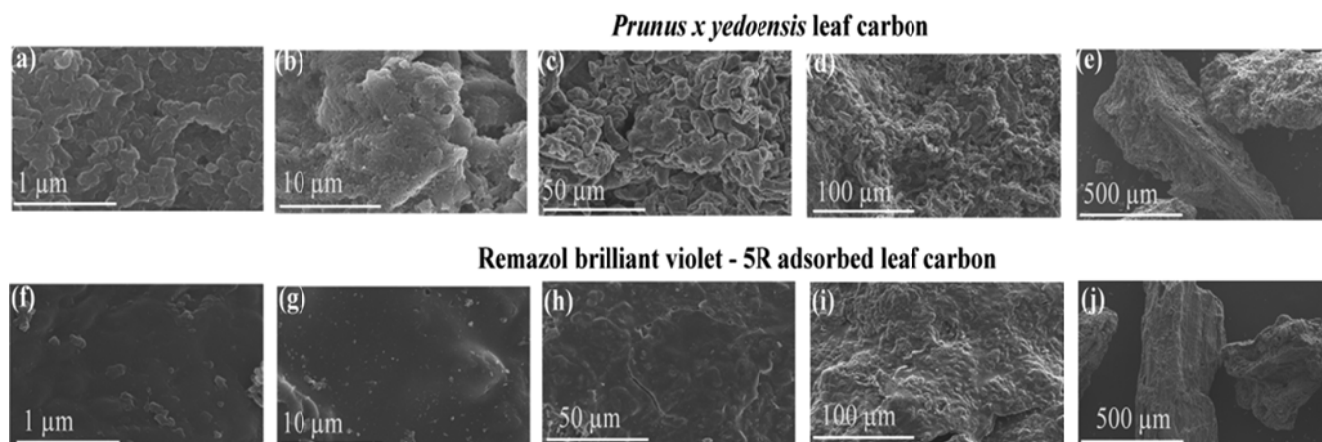


Fig. 1 — HR-FESEM image showing control carbon (a-e) and dye treated carbon (f-j).

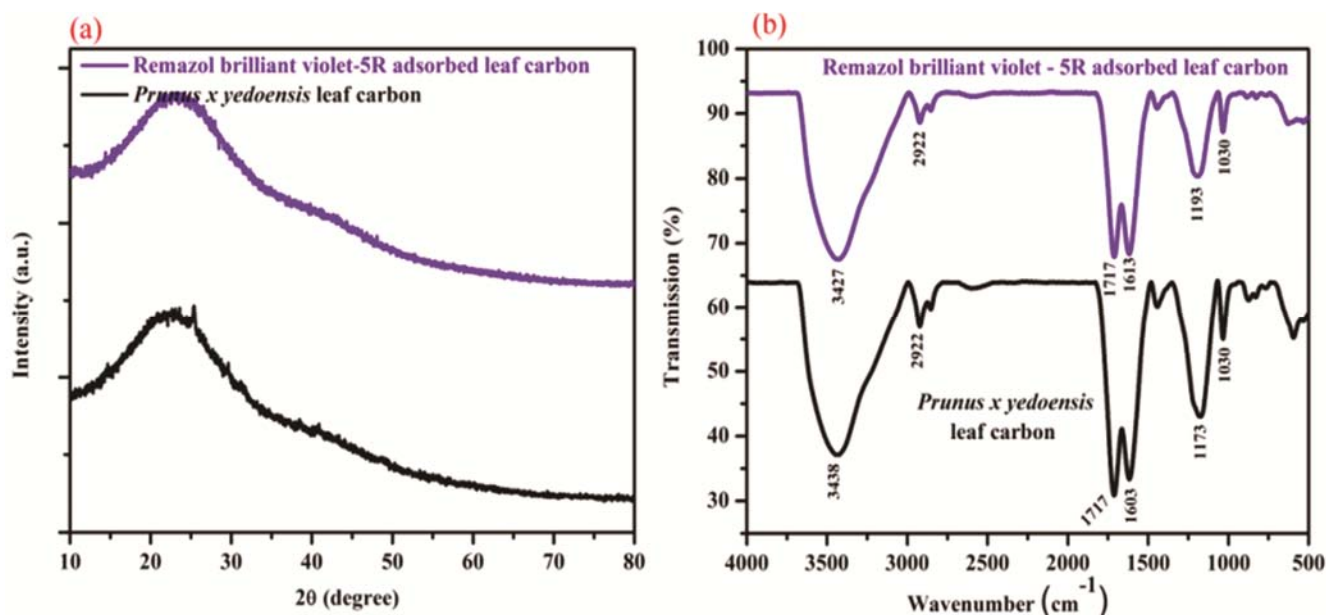


Fig. 2 — XRD (a) and FTIR-IR (b) spectra of control PYL carbon and dye treated PYL carbon.

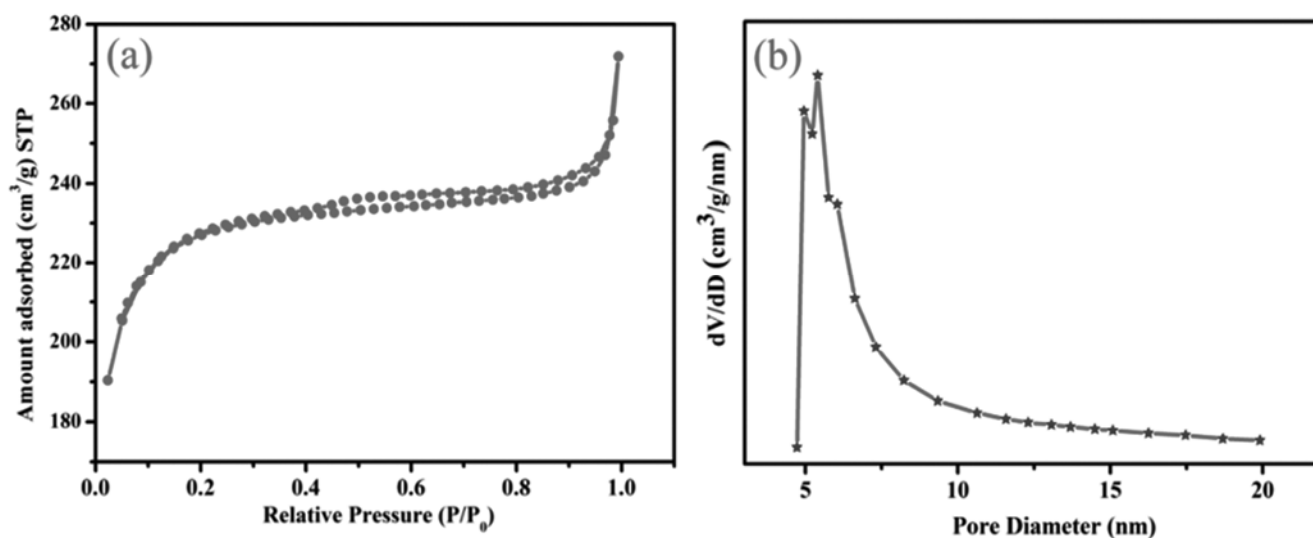


Fig. 3 — N<sub>2</sub> adsorption–desorption isotherms of control PYL carbon (a) and pore size (b).

size, also reveal macropores, mesopores and micropores. Our result was accordance with Qin *et al.*<sup>3</sup>, for the preparation of activated carbon from marigold straw to study the adsorption performance. The dye treated PYLC Fig. 1f–j shows clear evident, the surface of the prepared carbon material was filled with dye molecules is a evidence of potential adsorption. The energy-dispersive X-ray spectroscopy (EDS), the details of elemental composition of dye treated and un treated carbon was given in the supporting information as Fig. 1. Figure 2a shows the XRD pattern of dye treated and un treated PYL carbon.

PYLC were shown in Fig. 2b. The FT-IR spectra of PYLC showed several bands, corresponding to the region of 4000–500 cm<sup>-1</sup>. The broad band at 3438 and 3427 cm<sup>-1</sup> was assigned to adsorbed water for PYLC and dye adsorbed PYLC, respectively. A weak band at 2922 cm<sup>-1</sup> assigned to an asymmetrical and symmetrical stretch of CH<sub>3</sub>. Two sharp bands at 1717 and 1603 cm<sup>-1</sup> are corresponded to an aromatic carbon or carbonyls (stretch of C=C in aromatic rings and stretch of C=O), respectively<sup>13</sup>. These bands shifted to higher frequencies after adsorbing the dyes, which indicated an aromatic carbon or carbonyls could combine with the dye molecules on the surface of

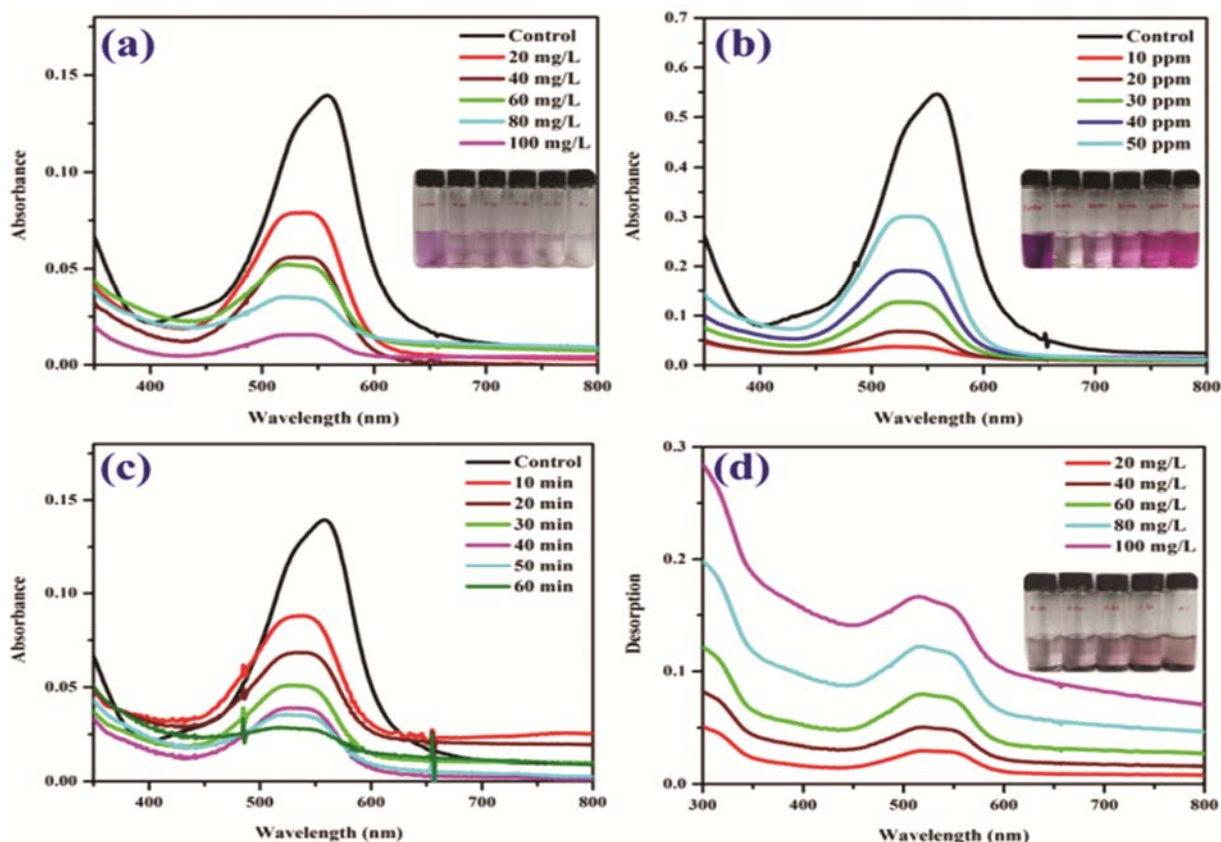


Fig. 4 — UV-Vis spectrum of RBV-5R absorption and desorption by PYL carbon (a) dose, (b) dye, (c) time and (d) desorption.

activated carbon<sup>13,14</sup>. The band at  $1137\text{cm}^{-1}$  of PYLC may belong to C-O stretching in alcohol or ether or hydroxyl groups. It could be seen that the absorbance peaks in dye-loaded PYLC shifted to  $1613$ ,  $1193$  and  $1030\text{cm}^{-1}$  for RBV dye. This shift in the absorption peak suggested the interactions of dye molecules with the functional groups of biosorbent<sup>13,15</sup>.

Figure 3a depicts the  $\text{N}_2$  adsorption-desorption results corresponded to the control carbon posed by type-I isotherms according to the IUPAC classification, illustrate the presence of mesoporous nature with  $270.8$  and  $240.6\text{m}^2\text{g}^{-1}$ <sup>16</sup>.

Figure 3b shows the pore-size distributions of the control carbon of PYLC. It was found that the PYLC are in porosity with sizes ranging from  $5.2$  to  $12.8\text{nm}$  indicating a well-developed mesoporous structure.

In our study, PYLC activated carbon showed the good catalytic activity for  $0.1\text{g}/25\text{mL}$  of dye solution Fig. 4a. Different dye concentration indicates the removal efficiency extremely decreased with increasing concentration above  $10\text{ppm}$  Fig. 4b. The dye concentration study had to  $100\%$  removal within  $60\text{mins}$  in the  $10\text{ppm}$  RBV-5R concentration Fig. 4c.

Figure 4d spectrum of desorption indicate  $20\text{mg/L}$  of dye adsorbed carbon desorbs in high amount.

They have finally been standardized of RBV-5R removal in first  $10\text{min}$  and then gradually increased until the equilibrium time was achieved in  $60\text{mins}$ . This carbon takes less contact time required to reach equilibrium as well as the higher adsorption. Earlier, most of these researches investigated and reports that the activated carbon with good ability for photocatalytic activity to adsorb and desorb RBV-5R<sup>13,16</sup>.

## Conclusion

In this study, Well porous activated carbon successfully made from *Prunus × yedoensis* with dye adsorption properties due to homogeneous shape, large pore volume with high specific surface area to remove RBV-5R.

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**References**

- 1 Yang N, Zhu S, Zhang D & Xu S, *Mater Lett*, 62 (2008) 647.
- 2 Malik P K, *J Hazard Mater*, 113 (2008) 88.
- 3 Qin C, Chen Y & Gao J M, *Mater Lett*, 135 (2014) 126.
- 4 Hussein M, Amer A A, El-Maghraby A & Taha N A, *J Appl Sci Res*, 3 (2007) 1358.
- 5 Chung J T, Hwang K J, Shim W G, Kim C, Park J Y, Choi D Y & Lee J W, *Mater Lett*, 93 (2013) 403.
- 6 Shawabkeh R A, Al-Harhi M & Al-Ghamdi S M, *Energ Sourc Part A*, 36 (2014) 103.
- 7 Velmurugan P, Shim J H, Kim K & Oh B T, *Mater Lett*, 174 (2016) 65.
- 8 Manikandan V, Velmurugan P, Park J H, Lovanh N, Seo S K, Jayanthi P, Park Y J, Cho M & Oh B T, *Mater Lett*, 185 (2016) 338.
- 9 Jain A, Aravindan V, Jayaraman S, Kumar P S, Balasubramanian R, Ramakrishna S, Madhavi S & Srinivasan M P, *Sci Rep*, 3 (2013) DOI: 10.1038/srep03002.
- 10 Karthick K, Dinesh C & Namasivayam C, *Sustain. Environ. Res*, 24 (2014) 148.
- 11 Bello O S & Ahmad Bulg M A, *J Sci Educ*, 21(2012) 395.
- 12 Sun D, Zhang Z, Wang M & Wu Y, *Am J Anal Chem*, 4 (2013) 26.
- 13 Gupta V K & Rastogi A, *J Hazard Mater*, 163 (2009) 402.
- 14 Liang S, Guo X, Feng N & Tian Q, *J Hazard Mater*, 174 (2010) 776.
- 15 Gao Y, Yue Q, Xu S & Gao B, *Mater Lett*, 14 (2015) 36.
- 16 Bello O S & Ahmad M A, *Chem Ecol*, 27 (2011) 492.