

## Nitrate removal from water phase using *Robinia pseudoacacia* bark for solving eutrophication

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**Abstract**—The bio-absorbent of *Robinia pseudoacacia* (*R. pseudoacacia*) bark was modified with sulfuric acid and their nitrate removal efficiency in water phase was investigated. At 2.5 ppm, the nitrate removal efficiency of *R. pseudoacacia* bark modified with 2, 4, 6, 8 and 10 M H<sub>2</sub>SO<sub>4</sub> was 54, 61, 69, 72 and 72%, respectively, and the maximum removal efficiency was increased by 100% as compared with the raw *R. pseudoacacia* bark. The XPS analysis results reveal that the acidic functional groups such as carboxylic, carbonyl and phenol groups were increased by 48% in the 8 M H<sub>2</sub>SO<sub>4</sub> modified *R. pseudoacacia* bark, and the specific surface area and the total pore volume increased by two-times to 4.94 m<sup>2</sup>/g and 0.0113 cc/g, respectively. In addition, 0.1 M sodium hydroxide performed as the best desorption agent for desorption rates using hydrochloric acid, sodium hydroxide and ethylenediamine tetraacetic acid (EDTA), in order to recover the nitrate. Collectively, these results could be employed as economical and practical engineering data for the development of nitrate removal process.

Keywords: *Robinia pseudoacacia* Bark, Nitrate Removal, Modified with Sulfuric Acid

### INTRODUCTION

Contamination of surface waters by nitrogen pollutants, such as nitrate, nitrite and ammonium, is increasing every year and has become a serious problem due to industrialization. Nitrate nitrogen exists in nature as NO<sub>3</sub><sup>-</sup> and is contained in most industrial wastewater like agricultural fertilizers, steel and plating wastes [1,2]. Once higher concentrations of nitrogen-containing industrial wastewater streams entering into water bodies like lakes, bays or oceans and their self-purification capability is exceeded, it causes issues like red tide, eutrophication, and dissolved oxygen deficiency [3]. The nitrate nitrogen absorbed into the body is known to form a carcinogenic N-nitroso compound, and it will cause cyanosis once it is ingested by infants [4,5]. To prevent this, the government is tightening regulations on the source of nitrogen pollution.

Physico-chemical processes like reverse osmosis, ion exchange, electro dialysis, and chemical treatment are used to remove nitrate nitrogen in water [6-10]; however, these processes are associated with the release of toxic substances due to use of additional chemicals so an additional treatment process is required [11]. To resolve these drawbacks, adsorption techniques using adsorbents like charcoal, chitosan, or rice husk are developed [12,13] since the adsorption method is simple, economical and easily regenerable. In recent years, studies have been carried out to remove harmful substances

present in the water by waste wood that has the advantage of reducing the quantity of waste generated by recycling waste wood [14-16].

So far, there has been no experimental study on the removal of nitrate ions present in water by using *R. pseudoacacia* bark. Especially, in the Chungbuk forest area of Korea, the recycling technology of wood wastes is urgently required since large amounts of *R. pseudoacacia* bark are generated as wood wastes. Also, the nitrate adsorption capacity of *R. pseudoacacia* bark containing viscous components is higher than other waste woods. In the present study, the *R. pseudoacacia* bark surface was chemically modified by sulfuric acid treatment and investigated for the removal nitrate ions present in water. We have tried to implement and develop eutrophication treatment technology, which effectively removes the nitrate ions in the water phase by using *R. pseudoacacia* bark.

### EXPERIMENTAL METHODS

#### 1. Materials

The *R. pseudoacacia* bark samples were collected as 2 mm pieces from the surface of the wood in the Chungbuk area. They were ground for 2 hours using a blender (FM-909T, Hanil Co., Korea). The particles were separated using a sieve vibrator (Analysette 3, Fritsch Co., Germany) and dried in a dryer (J-DSA1, Jisico Co., Korea) at 45 °C for 24 hours. Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 95%), potassium nitrate (KNO<sub>3</sub>, 99%), sodium hydroxide (NaOH, 98%), ethylenediamine tetraacetic acid (EDTA, 99%) and hydrochloric acid (HCl, 35-37%) were purchased from Samchun Chemical Company in Korea.

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## 2. Surface Modification of *R. pseudoacacia* bark

Various concentrations (1–10 M) of sulfuric acid solutions were prepared. 1 g of acacia bark was dispersed in to a 100 ml sulfuric acid solution and reacted at 90 °C and 120 rpm for 6 h. The modified *R. pseudoacacia* bark was washed with distilled water to a pH of 7, filtered and dried at 45 °C for 12 hours. The untreated *R. pseudoacacia* bark was named Raw-acacia and the *R. pseudoacacia* bark treated with sulfuric acid was named as 1, 2, 4, 6, 8 and 10 M H<sub>2</sub>SO<sub>4</sub> depending on the concentration of sulfuric acid solution.

## 3. Adsorption/Desorption Experiment

KNO<sub>3</sub> was used to prepare artificial wastewater solution which contains nitrate anions. 100 ppm of standard solution was prepared and of 2.5 and 5 ppm solutions were prepared by stepwise dilution from the standard solution. 0.1 g of *R. pseudoacacia* bark was added to 50 ml of 2.5 and 5 ppm solutions and reacted at 30 °C and 170 rpm in a shaking incubator (IS-971R, Jeitech Co., Korea). Samples were collected over a period of time.

To evaluate the regeneration of the adsorbent, desorption of nitrate ions was carried out using 0.1 M solution of different desorption reagents such as NaOH, EDTA, and HCl. After the adsorption process was completed, 0.1 g of the adsorbent was treated with 50 ml desorption reagent solution and the desorption efficiency was measured by using Eq. (1).

$$r(\%) = \frac{A_d}{A_a} \times 100 \quad (1)$$

where  $r$ =desorption rate (%),  $A_d$ =amount of nitrate nitrogen desorbed (mg/g),  $A_a$ =amount of nitrate nitrogen adsorbed (mg/g)

## 4. Analysis

The collected samples were subjected to solid-liquid separation using a centrifuge (Micro-12 Hanil, Korea) for 10 min at 4,000 rpm. The supernatant thus obtained was filtered using a 0.45 µm micro filter (MFS, Japan) and analyzed at a wavelength of 410 nm using a UV/VIS spectrophotometer (UV-1601PC Shimadzu), the concentration of nitrate was analyzed and the adsorption amount was calculated by Eq. (2) [17].

$$Q = \frac{(C_0 - C_e)V}{W} \quad (2)$$

$Q$ =amount of nitrate (mg/g) adsorbed on the adsorbent under adsorption equilibrium,  $C_0$ =initial nitrate nitrogen concentration before adsorption (mg/L),  $C_e$ =nitrate nitrogen concentration after adsorption equilibrium (mg/L),  $V$ =nitrate nitrogen volume (L),  $W$ = sorbent dose (g)

The surface area and pore volume of raw and acid treated *R. pseudoacacia* bark were analyzed by nitrogen sorption experiments at 77 K using ASAP 2020 (Micromeritics, US). The samples were pretreated at 423 K for 4 h and specific surface area and pore volume were calculated using the Brunauer-Emmett-Teller (BET) and density-functional theory (DFT) methods [18]. The changes in surface chemical properties before and after the acid treatment were investigated by X-ray photoelectron spectroscopy (XPS, MultiLab 2000, Thermo Electron Corporation, England).

## RESULTS AND DISCUSSION

### 1. Sorption/Desorption Characteristics of Nitrate

To evaluate the nitrate removal efficiency of modified *R. pseudoacacia* bark, the adsorption experiments were carried out on both raw and 1 M H<sub>2</sub>SO<sub>4</sub> treated *R. pseudoacacia* bark with two different concentrations (2.5 and 5 ppm) solutions. During the 20 minutes of these experiments, the removal of nitrate was carried out rapidly; and after 60 minutes minimal change in removal efficiency was observed due to reaching equilibrium. Fig. 1(a) shows the adsorption experiment results of 2.5 ppm solution. The removal efficiency of raw and 1 M H<sub>2</sub>SO<sub>4</sub> treated *R. pseudoacacia* bark was 27 and 48%, respectively and the adsorption amount was 0.33 and 0.65 mg/g, respectively. Fig. 1(b) shows the adsorption experiment results of 5 ppm solution. The removal efficiency of raw and acid treated *R. pseudoacacia* bark was 20 and 31%, respectively, and the adsorption amount was 0.49 and 0.85 mg/g, respectively. The acid treated *R. pseudoacacia* bark shows higher nitrate removal efficiency in 2.5 and 5 ppm nitrate.

Based on these results, the adsorbent was chemically modified by increasing sulfuric acid concentrations: 2, 4, 6, 8 and 10 M. As a result, removal efficiency of nitrate increased with an increased concentration of sulfuric acid, and the results are shown in Fig. 2. At 2.5 ppm concentration, the nitrate removal efficiency of the sor-

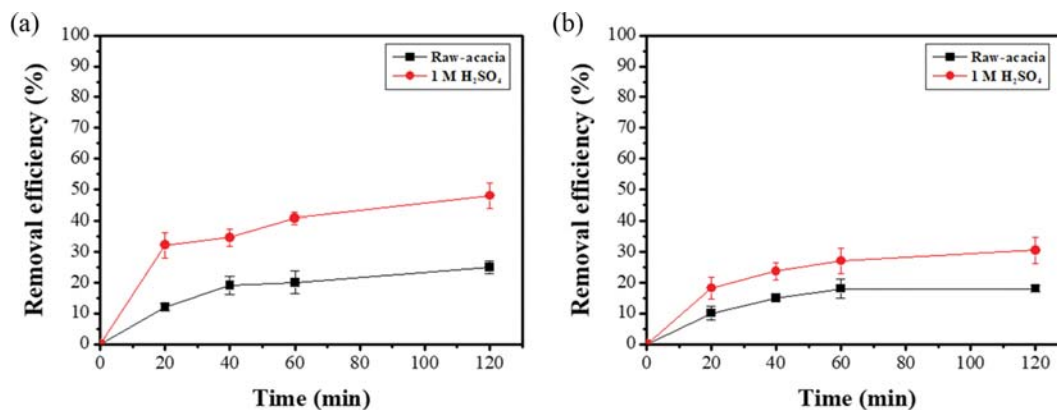


Fig. 1. NO<sub>3</sub>-N removal efficiency of untreated and 1 M H<sub>2</sub>SO<sub>4</sub> treated *R. pseudoacacia* bark at different initial concentrations; (a) 2.5 ppm, (b) 5 ppm.

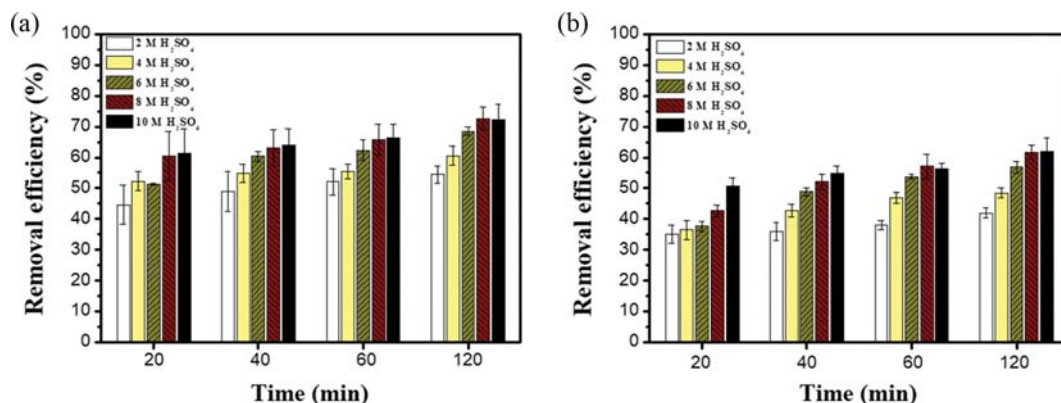


Fig. 2. Effect of H<sub>2</sub>SO<sub>4</sub> concentration on NO<sub>3</sub>-N removal; (a) 2.5 ppm, (b) 5 ppm.

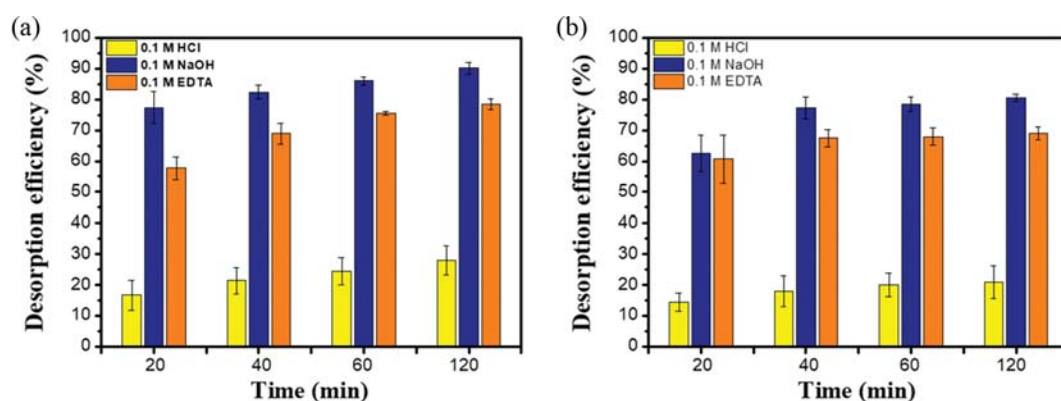


Fig. 3. Effect of various desorption agents on NO<sub>3</sub>-N; (a) 2.5 ppm, (b) 5 ppm.

bents modified with 2, 4, 6, 8 and 10 M H<sub>2</sub>SO<sub>4</sub> was 54, 61, 69, 72 and 72%, respectively. When the nitrate concentration was 5 ppm, the removal efficiency was about 42, 48, 56, 61 and 62% at each condition, and the maximum nitrate removal efficiency was increased to 62%. The higher the molar concentration of sulfuric acid used in the modification of *R. pseudoacacia* bark, the more efficient nitrate removal was observed. However, the removal efficiency of nitrate was relatively similar at higher concentration of 8 M H<sub>2</sub>SO<sub>4</sub>. Therefore, in this study, 8 M H<sub>2</sub>SO<sub>4</sub> was selected as the optimal concentration condition for the modification of *R. pseudoacacia* bark for nitrate adsorption. The amount of nitrate adsorbed on untreated *R. pseudoacacia* bark at 2.5 and 5 ppm concentrations was 0.33 and 0.49 mg/g, respectively. Whereas, the *R. pseudoacacia* bark modified with 8 M sulfuric acid shows 0.89 (2.5 ppm) and 1.53 mg/g (5 ppm). The amount of nitrate adsorbed on the modified sorbent was approximately increased by three-times.

To evaluate desorption characteristics of the 8 M H<sub>2</sub>SO<sub>4</sub> sample, desorption experiments as shown in Fig. 3 were carried out under the same conditions as in the adsorption at 2.5 and 5 ppm nitrate concentrations for 120 min. The nitrate desorption rates of the three reagents were as follows: NaOH > EDTA > HCl. NaOH showed a desorption rate of about 90%, and EDTA and HCl showed desorption efficiencies of 77 and 27%, respectively. Fig. 3(b) shows the desorption rate of *R. pseudoacacia* bark adsorbed at 5 mg/L nitrate nitrogen. NaOH showed the highest desorption rate (81%) followed

by EDTA (68%) and HCl (20%). Based on the experimental results, NaOH is the most effective nitrate desorbing agent.

## 2. Pore Characteristics of *R. pseudoacacia* bark by Chemical Modification

The nature of surface and pore characteristics such as specific surface area and total pore volume of the adsorbent greatly affects the adsorption characteristics of the adsorbate as well as its adsorption amount. As a result of the adsorption experiments, it was con-

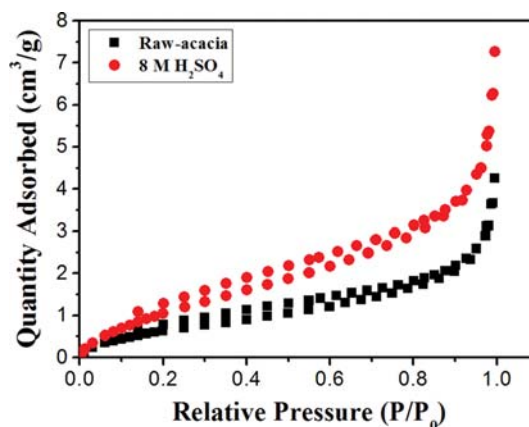


Fig. 4. Nitrogen isotherms of untreated and 8 M H<sub>2</sub>SO<sub>4</sub> treated *R. pseudoacacia* bark.

**Table 1. Pore characteristics of untreated and 8 M H<sub>2</sub>SO<sub>4</sub> treated *R. pseudoacacia* bark**

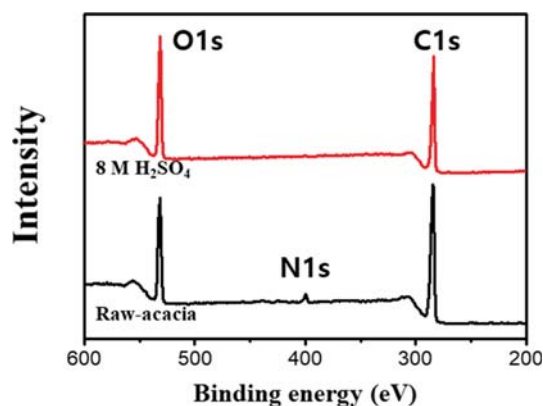
Samples	BET-specific surface area (m <sup>2</sup> /g)	Total pore volume (cc/g)	t-plot Micropore volume (cc/g)	Micropore V/ Total pore V (%)
Raw-acacia	2.6628	0.0065	0.0003	0.0062
8 M H <sub>2</sub> SO <sub>4</sub>	4.9394	0.0113	0.0008	0.0105

firmly that the nitrate removal efficiency was the best when it was modified with 8 M H<sub>2</sub>SO<sub>4</sub>. Therefore, this sample was selected as the acid treated representative sample and compared with the raw sample. Fig. 4 shows the N<sub>2</sub> sorption isotherms of raw and 8 M H<sub>2</sub>SO<sub>4</sub> at 77.4 K and the BET surface area and micro pore volume values are given in Table 1. The adsorption isotherms are of Type II, and according to the IUPAC classification it indicates the multi-layer adsorption on nonporous materials [19,20]. In addition, the nitrogen adsorption amount of the 8 M H<sub>2</sub>SO<sub>4</sub> was slightly increased compared with the raw sample, but the overall pore structure was not significantly changed. As shown in Table 1, the non-porous *R. pseudoacacia* bark exhibited a specific surface area of 2.66 m<sup>2</sup>/g, whereas 8 M H<sub>2</sub>SO<sub>4</sub> showed a specific surface area of 4.94 m<sup>2</sup>/g. The specific surface area and total pore volume were increased by two-times after the acid treatment.

### 3. Surface Characteristics of *R. pseudoacacia* bark by Chemical Modification

The XPS analyses were carried out on raw and 8 M H<sub>2</sub>SO<sub>4</sub> *R. pseudoacacia* bark samples and representative C (1s), N (1s) and O (1s) spectra are shown in Fig. 5. The surface atomic composition (%) values are presented in Table 2. In the case of raw *R. pseudoacacia*, the percentage of carbon, oxygen and nitrogen was 77, 21 and 2%, respectively. However, after the acid treatment, the carbon content decreased to 68% and the relative oxygen content increased to 31%, respectively. Nitrogen peak in untreated *R. pseudoacacia* bark was decreased to 0.29% after acid treatment. In general, acidic functional groups are known to be effective for nitrate ion adsorption [21]. As shown in Fig. 2, nitrate removal efficiency appears to be influenced by acidic functional groups on the adsorbent surface after acid treatment.

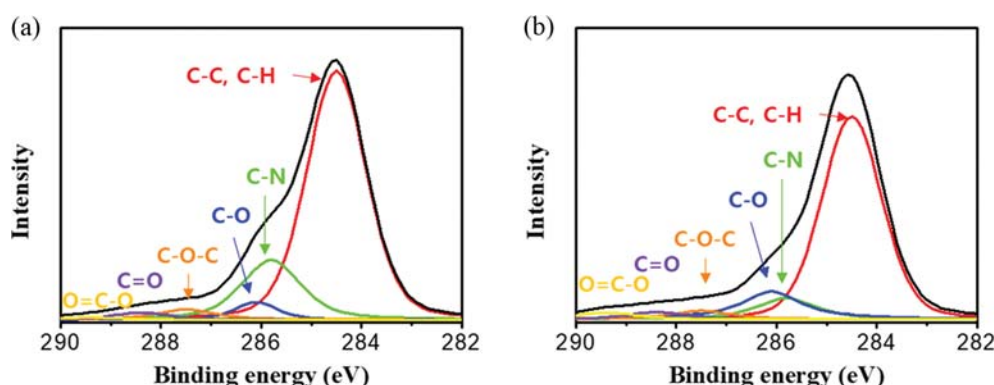
The deconvolution of The C (1s) peak was obtained by the pseudo-Voigt Eq. (3). In this equation, F (E) denotes the intensity at energy E, H denotes the height of the peak, S denotes the shape

**Fig. 5. XPS wide scan spectra of untreated and 8 M H<sub>2</sub>SO<sub>4</sub> treated *R. pseudoacacia* bark.****Table 2. XPS survey analysis of untreated and 8 M H<sub>2</sub>SO<sub>4</sub> treated *R. pseudoacacia* bark**

Sample	Elemental contents (atomic%)			O/C (%)
	C (284.5 eV)	O (532.2 eV)	N (400.6 eV)	
Raw-acacia	76.56	21.20	2.24	14
8 M H <sub>2</sub> SO <sub>4</sub>	68.39	31.31	0.29	45

function associated with the symmetry and Gaussian-Lorentzian mixing ratio, E<sub>0</sub> denotes the center value of the peak, FWHM denotes the half-Value [22].

$$F(E) = H \left[ (1-S) \exp \left( -\ln(2) \left( \frac{E-E_0}{FWHM} \right)^2 \right) + \frac{S}{1 + \left( \frac{E-E_0}{FWHM} \right)^2} \right] \quad (3)$$

**Fig. 6. C1s core level spectrum of untreated and 8 M H<sub>2</sub>SO<sub>4</sub> treated *R. pseudoacacia* bark; (a) Raw-acacia, (b) 8 M H<sub>2</sub>SO<sub>4</sub>.**

**Table 3. C1s peak parameters of untreated and 8 M H<sub>2</sub>SO<sub>4</sub> treated *R. pseudoacacia* bark**

Component	Peak position (eV)	Area (%)	
		Raw-acacia	8 M H <sub>2</sub> SO <sub>4</sub>
C(1) C-C/C-H	284.5	71.1	61.4
C(2) C-N	285.5	10.8	8.5
C(3) C-O	286.1	11.9	16.9
C(4) C-O-C	287.5	3.4	5.7
C(5) C=O	288.4	2.1	4.9
C(6) O=C-O	289.4	0.7	2.6

The results of the C (1s) main peak segmentation are shown in Fig. 6. Table 3 shows the types of functional groups, the position and the area (%) of the peaks. After acid treatment, the C-N content decreased to 8.5%, while the C-O content increased to 16.9%, as compared to the untreated sample. It is generally known that functional groups such as carboxylic group (-COOH), carbonyl group (-C=O) and phenol group (-C-OH) influence the nitrate adsorption [21]. Oxygen functional groups were introduced into the surface of the *R. pseudoacacia* bark during the surface treatment, and it was suggested that the introduced oxygen functional groups improved the nitrate adsorption efficiency.

### CONCLUSION

A modified *R. pseudoacacia* bark adsorbent was prepared by sulfuric acid treatment, and its ability to remove nitrate from aqueous solutions of different concentrations was evaluated. All the *R. pseudoacacia* barks samples treated with sulfuric acid were higher than the untreated *R. pseudoacacia* bark at 2.5 ppm of nitrate ions, and their removal efficiencies improved to 72%. This phenomenon appears to be attributed to the removal of more adsorbed nitrate due to functional groups such as carboxylic group (-COOH), carbonyl group (-C=O) and phenol group (-C-OH) introduced on the surface of *Robinia pseudoacacia* bark after acid treatment. Furthermore, the nitrate desorption rates of the three desorption reagents were as follows: NaOH>EDTA>HCl, when comparing the nitrate desorption efficiency. Thus, these experimental results can be useful in implementing and developing eco-friendly water treatment techniques to remove and recover the nitrate from aqueous solutions.

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