Biosorption of Cr (VI) ions by Ficus religiosa barks: Batch and continuous study

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Abstract. In the present research, Ficus religiosa Bark (FRB) is used as an adsorbent for the removal of heavy metal Cr (VI) ions. This Ficus religiosa Bark was characterized by Scanning Electron Microscope, Fourier transform infrared Spectroscopy, Thermo Gravimetric Analyzer and the results showed that activated adsorbent have high adsorption capacity and withstand even in high temperature. Batch and Continuous experiments were conducted to determine the effect of various parameters such as pH, contact time, adsorbent dose and initial metal concentration. The biosorption followed pseudo first order kinetic model. The adsorption isotherms of Cr (VI) on Ficus religiosa fitted well with the Temkin model. In Batch study, maximum biosorption capacity of Cr (VI) was found to be 37.97 mg g⁻¹ (at optimal pH of 2, adsorbent dosage of 0.3 grams and concentration of Cr (VI) is100 mg L⁻¹). The Continuous mode of study shows that 97% of Cr (VI) ion removal at a flow rate of 15 ml min⁻¹. From the results, selected *Ficus religiosa Bark* has the higher adsorption capacity for the removal of Cr (VI) ions from wastewater.

Keywords: biosorption; Cr (VI); Ficus religiosa Bark; kinetics; Temkin model; wastewater treatment

1. Introduction

Water plays a vital role in human life survival because the uses of water include drinking, agricultural, environmental, household and industrial activities (Martins *et al.* 2013). But there is 97% of the water on the Earth is salt water and only 3% is fresh water; slightly over two third of this is frozen in glaciers and polar ice gaps. The remaining fresh water is found mainly as ground water, with only a small fraction present above the ground or in the air. The quality of water resources is deteriorating day by day due to the population growth, the rapid development of industrialization, agricultural activities, and other geological and environmental changes World Health Organization (2011). In the current scenario, it is very important to maintain the quality of the water and to make ways for the reuse.

The development of industries, result in the release of various toxic substances and also most of the heavy metals into the water sources Masoumi and Ghaemy (2014), it creates a water pollution. Therefore, drinking water scarcity has become a critical issue worldwide the continuous release of heavy metals and organic compounds into the environment is causing growing concern tothe whole world (Pal *et al.* 2014). Heavy metals are particularly problematic because, unlike most organic contaminants, they are non-biodegradable and can accumulate in living tissues, posing a greater threat to both human health and ecological environment (Yuan *et al.* 2013). It is the dutyof researchers to find the solution for protecting resources. Chromium

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(VI) occurs in higher concentration in the wastes from leather industries, dyes, paints, paper industries, etc. and ranges from varies from 10 to 3000 mg L⁻¹Li (2013). The maximum allowable level of chromium in the drinking water is 0.05 mg L⁻¹ (Gong et al. 2013). Over exposure of chromium in the atmosphere cause to irritation of the skin and lung Carcinoma (Kaya et al. 2014). Therefore, several treatment techniques have been developed forthe removal of toxic metals from an aqueous solution Fenglian Fu and Qi Wang (2011) which includes chemical precipitation, ion-exchange, adsorption, membrane filtration, coagulationflocculation, flotation and electrochemical method (Kim et al. 2013). Even though these technologies help in the removal of toxic metals they all have its own drawbacks. Some of the disadvantages include higher initial concentration, complication in sludge disposal and other cost- related problems. Unlike other technologies, the adsorption and membrane filtration is a promising method for the removal of toxic metal ions (Kyzas et al. 2011). The adsorption includes advantages like easy handling, low operation cost, more efficient and produces high-quality effluent (Wanga et al. 2014). Wastewater even with minimal metal concentration can also be treated by adsorption method (Gao et al. 2014). The preference of bio sorbent is highly targeted due to their high removal efficiency (Abbas et al. 2014) and mainly low cost Saleh and Vinod Kumar Gupta (2014). In the adsorption process, the most used activated carbons are generally expensive since their parent materials are high in cost and also for the regeneration process (Lin et al. 2014). Due to this, researchers have focused on the production of low-cost activated carbons which includes high carbon and low inorganic content Wan Ngah and Hanafiah (2008). There

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Fig. 1 Flow diagram of Activated FRBs preparations method

are many bio-based agricultural wastes which fulfill these requirements. Some of the agricultural wastes which are converted as activated carbon include rice husk and straw, coconut shell, hazelnut shell, apricot stone, cornelian cherry, leaves, date palm seed, almond shell, tamarind wood, peach stone, baelfruit shell, olive bagasse, sugarcane bagasse, etc. (Qaiser *et al.* 2009). In present work, FRBs (*Ficus religiosa Barks*) in free and immobilized forms are utilized for the treatment of removing heavy metal ions from industrial wastewater is investigated.

2. Materials and methods

2.1 Chemical preparation

The chemical required for the research work, Potassium dichromate, Sulphuric acid was received from E. Merck, India. The stock Cr (VI) solution of 1000 mg L^{-1} concentration was prepared by dissolving 2.82 g of potassium dichromate (E. Merck, India) in 1L of distilled water. Distilled water was used for the dilution of the stock solution and the desired concentrations (25-150 mg L^{-1}) were prepared.

2.2 Preparation of biosorbent

FRB was collected locally, from SVCE (Sri Venkateswara College of Engineering) campus, Sriperumbudur, Tamilnadu. These Barks were washed, repeatedly with distilled water to remove dust and soluble impurities and were allowed to dry at room temperature. The dried Bark was converted into fine powder by grinding in a mechanical grinder. The powder was sieved and the size fraction 60–80 mm was used in the experiments. This powder was soaked in $0.1M H_2SO_4$ for 24 hr (50 g FRBs powder was soaked per liter). The aim of acid treatment is to expose the binding sites of biosorbent and to increase removal capacity of adsorbent by this pretreatment. The bio sorbent was filtered and washed with distilled water to remove acid contents. The washing was continued till the pH of the filtrate was close to 7. It was first dried at room temperature and then in a micro oven at 105°C for 2 hours to completely remove moisture (Qaiser *et al.* 2009). This adsorbent was stored in a plastic container and it was named as FRBs which was used for the effective removal of Cr (VI) in the adsorption process.

2.3 Characterization of biosorbent

FTIR technique can be significantly used to categorize the diverse functional groups present on the surface of the adsorbent material (FRBs) and also the communication between the metal ions and the chemical boundaries on the surface of the adsorbents can be recognized by using the FTIR technique (Chao et al. 2014). This study was carried out by using attenuated total reflectance in the range between 4000-100 cm⁻¹. SEM analysis is used to identify the surface morphology of the adsorbent material. Biosorption is mainly depended on the number of pores on the surface of the adsorbents. Large cavities and more pores are the important factors for the absorption of metal ions. The surface morphology of the FRBs was measured using a Quanta 200 FEG scanning electron microscope (Chao et al. 2014). The working distance of 100 µm was used at an accelerating voltage of 30 kV. Thermo gravimetric analysis (TGA) is a method of thermal analysis in which thermal stability of adsorbent was determined by mass loss. The concentration of Cr (VI) ions in the supernatants were analyzed by using the atomic absorption spectrophotometer (AAS) (AA 301 Model, Nasik, India).



Fig. 2 Schematic diagram of a continuous adsorption column with membrane filtration (Two tier MBR- module)



Fig. 3 FTIR results of Activated FRBs before and after adsorption at 32°C, pH-7 and batch studies

2.4 Batch adsorption

The batch adsorption studies were carried in a 100 mL Erlenmeyer flask. The adsorption process was worked out by changing different parameters such as Cr (VI) ions concentration in aqueous solution, contact time, adsorbent dosage and also the solution pH of the aqueous solution. These varying experiments were performed to study the removal efficiency of Cr (VI) in the FRBs from the aqueous solution by the adsorption process. During the adsorption process to maintain the optimumpH level, 0.1 M NaOH or 0.1 M HCl was added to the aqueous solution (He et al. 2014). 100 mL of the desired Cr (VI) concentration ion solution was taken in a 100mL Erlenmeyer flask and the FRBs were weighed in desired quantity and was added to the Cr (VI) ion solution. After that, the flask was kept in a shaking incubator at a selected controlled temperature with a constant speed of 100 rpm. In another sort, the time was varied from 10 to 150 min. After the adsorption period, the solution is filtered and the Cr (VI) ions concentration was analyzed by using an atomic absorption spectrophotometer (AAS) (301 Model, Nasik, India).

2.5 Continuous adsorption study

Continuous biosorption experiment (Fig. 2) was carried out in 2-Tiered Pilot MBR Module (Hollow fiber). Initially synthetic Cr (VI) ion concentrated solution was prepared from different range from 25 to 125 mgl⁻¹ and loading rate of FRBs also varies. Before starting continuous column operation, reactor was cleaned with water several times and leakage checks also done. Prepared aqueous Cr (VI) and FRBs was passed into the continuous column and the holding capacity of the tank is 15L. In that column, Aerator was placed at the bottom. This aeration mainly helps for FRBs circulation and more adsorption of heavy metal Cr (VI) ion takes place. Inlet flow rate (5-15 ml min⁻¹) set from a tank at certain height through roto meter and outlet treated solution carry out by a peristaltic pump at a certain flow rate. Initial metal ion concentration, adsorbent dosage effect, and flow rate checked through the continuous column were analyzed by using Atomic Absorption Spectrophotometer (AAS) (AA 301 Model, Nasik, India).

3. Results and discussion

3.1 Characterization of the biosorbent

The FTIR study of FRBs is studied before and after the adsorption process. An intense broad band is observed at 480 cm⁻¹ (Fig. 3) which indicates the presence of -OH and -NH Group (Salam *et al.* 2012). The peak at 470 cm⁻¹ is the indication of C=N bending which further confirms the presence of amine groups. The broad band 460 cm⁻¹, 455 cm⁻¹ get (Chao *et al.* 2014) lowered which indicates that hydrogen bond interactions could exist between FRBs and Cr (VI). The Cr (VI)-loaded spectrum further suggests that the functional groups play a major role in the process of Cr (VI) adsorption on FRBs.

Fig. 4 shows the SEM images (a and b) it can observe that the surface of the adsorbents was irregular and porous. This shows that the adsorbent has a sufficient morphology



Fig. 4 SEM micrograph of FRBs



Fig 5 TGA result of FRBs activated adsorbent

for the adsorption process. The irregular surface and the porous nature allow the metal ion Cr (VI) to accumulate onto the functional groups which are present inside the walls of the adsorbent surface. The functional groups which are present on the surface of the adsorbent are already mentioned under the FTIR studies.

Fig. 5 shows the thermo gravimetric analysis (TGA) inference; the stage I (i.e. from 35° to 250°C), the water on the surface and external water bounded to the surface by surface tension were lost. The second stage occurred from 250°C to 400°C which is known as devolatilization stage. During this stage, volatile compounds were gradually released from the biomass and hence resulted in the major weight loss. Stage II, which occurs from 370°C to 400°C the major weight loss was due to slow decomposition of the remaining residue from stage II. Hence, TGA results proved that prepared adsorbent able to withstand at high temperature up to 300°C for wastewater treatment.

3.2 Batch biosorption experiment

3.2.1 Effect of pH on adsorption

The initial pH value of the aqueous solution is an important parameter in the adsorption process. The Cr (VI) adsorption capacity on FRBs is plotted as a function of the initial pH value in Fig. 6. The results showed that the adsorption capacity gradually increases as the pH value of the solution decreases from 12 to 2. The Cr form only requires a cationic site of FRBs for adsorption at low pH value. On the other hand, with increasing pH, the amount of OH- available is gradually increased and the cationic charges of the amine functional groups (-NH⁺³) on the surface of the FRBs are consumed. Therefore, the adsorption capacity with respect to Cr (VI) gradually decreases with increasing initial pH. The maximum biosorption Capacity of chromium was at pH of 2. This phenomenon stated that the maximum removal of Cr (VI)



Fig. 6 Effect of pH on Cr (VI) biosorption. Initial conc. = 100mg L^{-1} , 0.3g in100 ml, 30°C, 100 rpm, 120 min



Fig. 7 Effect of Equilibrium time on Cr (VI) biosorption on various metal ions concentration (pH=2, 0.3g in 100 ml, 30°C, 100 rpm, 120 min)



Fig. 8 Effect of FRBs dosage on Cr (VI) biosorption Initial conc. = 100 mg L^{-1} pH=2, T=30°C, 100 rpm, 120 min)

ions is decreasing with increasing the pH, therefore the adsorption studies of Cr(VI) ions for pH > 4.0 is not recommended.

3.2.2 Determination of equilibrium time

The Fig. 7 shows the percentage removal as a function of the equilibrium time for sorption of Cr (VI) ion on FRBs carried out in a batch process. About 0.3 grams of FRBs added to 100 ml Cr (VI) ion (25, 50, 75, 100, 125 mg L⁻¹) at pH=2 for 120 min. It was shaken at 100 rpm and samples were collected at different time intervals. And filtrate analyzed by using the Atomic Absorption Spectrophotometer (AAS) (AA 301 Model, Nasik, India). Increasing chromium concentration from 25 mg/l upto 100 mg/l removal efficiency is high after that removal efficiency will be decreased. 90% of removal attained at 100 min and concentration becomes constant after 120 min. Therefore 2 hours sufficient for attaining equilibrium condition.

3.2.3 Effect of dosage

The adsorbent dose is the important process parameter for the removal of Cr (VI) ions from the aqueous solution in a batch adsorption experiment. These functional groups interact with metal ions during the adsorption process and observe the metal ions in their surface Milicevic (2012). The effect of adsorbent material FRBs was studied by contacting the initial metal ion concentration 100 mg L⁻¹ with the varied amount of adsorbents (0.1, 0.2, 0.3, 0.4, 0.5, grams) at pH = 2.0 for 120 min at 30° C. The suspensions were centrifuged and the concentration of Cr (VI) ions in the supernatants was analyzed by using the atomic absorption spectrophotometer (AAS) (AA 301 Model, Nasik, India). Theresults are mentioned in the figure 8, clearly showed that the removal percentage of Cr (VI) ions were increased with the increase in the adsorbent dosage due to the more availability of active sites on the surface of the adsorbents Milicevic (2012). The percentage removal of Cr (VI) ions was reached a maximum when the amount of adsorbent dose was increased from (0.1 to 0.5 for FRBs). As a further increase in the adsorbent dose, the percentage removal of Cr (VI) ions reaches nearly the constant value because of the low driving force, low equilibrium concentration and unavailability of active sites leading to the refuse in the total surface area (Ding et al. 2014). The maximum percentage removal of Cr (VI) ions was found to be 93% for 0.3 grams FRBs.

3.2.4 Adsorption isotherms

Adsorption isotherm plays a vital role in the adsorption process. These equilibrium data gives information about the amount of FRBs required for removing a unit mass of Cr (VI) ions under the system conditions [pH = 2, Temperature]= 30° C, FRBs Dosage = 0.3 grams, time = 120 min, Concentration = 25,50,75,100,125 mg L⁻¹]. Figs. 9-11 indicates the Langmuir, Freundlich and Temkin adsorption isotherm models were employed to fit the data observed from the effect of initial Cr (VI) ions concentration studies Salam (2018). The Linearized Form of Langmuir equilibrium isotherm equation can be written as Eq. (1) and graph plot between ln ce versus ce/qe Javadian (2014). The Linearized Form of Freundlich equilibrium isotherm equation can be written as Eq. (2) and Graph plot between log qe versus log ce. Javadian (2014). Eq. (3) is known as Temkin equilibrium isotherm form and graph plot between $\ln c_e$ versus q_e .



Fig. 9 Langmuir Isotherm plot for Cr (VI) biosorption (Initial conc. = 25-125mg L⁻¹, 0.3g in 100ml, 30°C, 100 rpm, 2 hr)



Fig. 10 Freundlich Isotherm plot for Cr (VI) biosorption (Initial conc. = 25-125mg L⁻¹, 0.3g in 100ml, 30°C, 100 rpm, 2 hr).



Fig. 11 Temkin Isotherm plot for Cr (VI) biosorption. Initial conc. = 25-125mg L⁻¹, 0.3g in 100ml, 30°C, 100 rpm, 2 hr

Table 1 Langmuir, Freundlich, and Temkin model parameters

S.No	LangmuirIsotherm	FreundlichIsotherm	Temkin Isotherm
1	R ² =0.968	R ² =0.960	R ² =0.999
2	Xm=15.873	N=2.288	Bj=7.259
3	b=2.079	Kf=5.640	

$$\frac{c_{\varepsilon}}{q_{\varepsilon}} = \frac{1}{X_{mb}} + \frac{c_{\varepsilon}}{X_{m}} \tag{1}$$

where q_e is the amount of metal ions adsorbed onto the unit mass of the adsorbent to form a complete monolayer on the surface *b* is the equilibrium constant related to the affinity of the binding sites for the metals X_m is determined from a linearized form equation

$$\log q_e = \log k_f + 1/n \log c_e \tag{2}$$

where k_f and 1/n are the Freundlich constant characteristics of the system

$$q_e = b_j \ln(K_t C_e) \tag{3}$$

 K_t is the equilibrium binding constant (ml mol⁻¹) corresponding to the maximum binding energy and constant b_j is related to the heat of adsorption.

From the Table 1, R²=0.999 correlation coefficient obtained from Temkin isotherm is higher than both Langmuir and Freundlich adsorption isotherm value. Therefore it indicates that multilayer adsorption and heat of adsorption decreases linearly with increasing coverage.

3.2.5 Adsorption kinetic experiments

Two different kinetic models namely pseudo-first-order and pseudo- second-order have been used to test the validity of the experimental adsorption data. These kinetic experiments were carried out by changing the contact time from 10 to 120 min with a constant 30°C temperature. The adsorbents were added to the solution of varying Cr (VI) ion concentration (25 - 125 mg L⁻¹) taken in 100 mL Erlenmeyer conical flasks. After reaching the equilibrium time the Cr (VI) ion solutions were analyzed by using the atomic absorption spectrophotometer (AAS) (AA 301 Model, Nasik, India) to find the concentration of Cr (VI) ions in the supernatants. Using the obtained data the adsorbed amount of Cr (VI) ions by the adsorbent at varying contact time was calculated using the formula (Ding *et al.* 2014),

$$q_t = \frac{(c_0 - c_t)v}{m} \tag{4}$$

where q_t is the amount of Cr (VI) ions adsorbed onto the adsorbent at any time t (mg g⁻¹), qe the amount of Cr (VI) ions adsorbed onto the adsorbent at equilibrium t (mg g⁻¹) C_0 is the initial concentration of Cr (VI) ions (mg L⁻¹), C_t is the concentration of Cr (VI) ions measured at time interval t (mg L⁻¹), m is the mass of the adsorbent (g) and V is the volume of the Cr (VI) ions solution (L).



Fig. 12 Pseudo first order kinetics plot for Cr (VI) biosorption Initial conc. = 25-125mg L⁻¹, 0.3g in 100ml, $30\circ$ C, 100 rpm, 2 hr



Fig. 13 Pseudo second order kinetics plot for Cr (VI) biosorption Initial conc. = 25-125mg L⁻¹, 0.3g in 100ml, $30\circ$ C, 100 rpm, 2 hr

Pseudo-first order kinetic model (Lagergren 1898) equation Vijayaraghavan and Yun (2008) is expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_s - q_t) \tag{5}$$

Pseudo-Second-Order Model:

$$\frac{dq_t}{dt} = k_2 (q_\theta - q_t)^2 \tag{6}$$

where k_1 and k_2 is the pseudo-first order (min⁻¹) and second order kinetic rate constant (g mg⁻¹ min⁻¹), t is the time (min), R² is the Correlation coefficient. A Graph plot between ln (q_e - q_t) versus t (min) for pseudo-first order kinetic rate and another Graph plot between t/qt versus t (min) for pseudofirst order kinetic rate determining. The Figs. 12 and 13 shows the pseudo order kinetics for the system and Table2-3 shows the kinetics parameters, R² = 0.978, from the Table 2, indicate that sorption followed by Pseudo-first order kinetic.



Fig. 14 Effect of FRBs dosage on Cr (VI) biosorption (Initial conc. = 100mg L^{-1} , pH=2, 30 °C, 15 ml min⁻¹

Table 2 Pseudo-first order kinetic parameters

Pseudo-first order kinetic	25 ppm	50 ppm	75 ppm	100 ppm
\mathbb{R}^2	0.926	0.944	0.956	0.978
q _e	2.601	3.289	3.501	3.817
K1	0.497	0.462	0.527	0.493

Table 3 Pseudo-second order kinetic parameters

Pseudo-second order kinetic	25 ppm	50 ppm	75 ppm	100 ppm
\mathbb{R}^2	0.907	0.937	0.945	0.944
q_e	10	18.86	27.02	35.71
K1	0.0027	0.0018	0.0013	0.00106

3.3 Continuous column experiment:

3.3.1 Effect of Dosage

For continuous column, the effect of adsorbent material FRBs was studied by contacting the initial metal ion concentration 100 mg L⁻¹ with the varied amount of adsorbents (2-12 grams) at pH = 2.0 for 120 min,15ml/min at 30°C. The outlet of the column is treated Cr (VI) ions from the Two Tier MBR module was analyzed by using the atomic absorption spectrophotometer (AAS) (AA 301 Model, Nasik, India). The plot between Adsorbent Dosage versus removal (%) of Cr (VI) shows in the Fig. 14. The percentage removal of Cr (VI) ions was reached a maximum when the amount of adsorbent dose was increased from (2-12 grams for FRBs). As a further increase in the adsorbent dose, the percentage removal of Cr (VI) ions reaches nearly the constant value. The maximum percentage removal of Cr (VI) ions was found to be 98% for FRBs.

3.3.2 Effect of concentrations

The effect of Cr (VI) ion concentration on adsorption was studied by pumping Cr (VI) solution at a flow rate of 15 mL min⁻¹ with dosage 10 grams adsorbent into Continuous Column. The Cr (VI) ion concentration used



Fig. 15 Effect of Cr (VI) ion concentration (FRBs=10 grams, pH=2, T=30°C,100 rpm, 120 min)



Fig. 16 Effect of Cr (VI) ion concentration (FRBs=10 grams, pH=2, T=30°C, 100 rpm, 120 min)

was 100,150,200 mg L⁻¹. Final Concentrations of outlet collected through MBR module and examined through was analyzed by using the atomic absorption spectrophotometer (AAS) (AA 301 Model, Nasik, India). Fig. 15 is the breakthrough curves were obtained by plotting the experimental data between removal percentage and time. At 100 mg/L gives maximum removal percentage, attained 90% at 95 mins and maximum removal is 97.67%, 120 mins.

3.3.3 Effect of flow rate

In industries scale, the flow rate is an important factor for continuous Treatment of wastewater. Theeffect of flow rate on Cr (VI) ions biosorption was studied by varying the inlet and outlet flow rate equally from 5 to 15ml/min[100 mg L⁻¹,pH=2,30°C]. Column Capacity is 15 L and10 grams adsorbent dosage. At a constant interval of time sample was outlet sample was analyzed by the atomic absorption spectrophotometer (AAS) (AA 301 Model, Nasik, India). The plotted between time versus removal (%) for various flow Shows in the Fig. 16. From the graph 15 ml/ min gives maximum removal of Cr (VI) other than 5 and 10 ml min⁻¹.

4. Conclusions

From the research work, we concluded Activated Ficus Religiosa Bark (FRBs) is a novel biosorbent and possess large efficiency to adsorb Cr (VI) ions from aqueous solution. The characterization studies were examined by FTIR, SEM and TGA results. The biosorption properties of FRBs for removal of Cr (VI) ions were investigated in Batch and continuous system. The maximum removal was Cr (VI) ions by activated FRBs observed at 30°C. In the kinetic adsorption experiments, the adsorption data were successfully fitted by the Pseudo-First order model for Cr (VI) ions. The Temkin isotherm equation $[R^2=0.99]$ was more accurate than Langmuir and Freundlich equation to fit the adsorption characteristics under different initial metal concentration in the isotherms adsorption experiments for the Cr (VI) ions biosorption. The maximum biosorption capacity of Cr (VI) ions was 37.97 mg g⁻¹ at optimal pH of 2 for chromium ions respectively. The Continuous Column experiments were analyzed at different flow rates, dosage, and Concentration. Finally, the result of continuous Experiment study shows that 97% biosorption of Cr (VI) ions from the aqueous solution obtained at a concentration of 100 mg L⁻¹ and a flow rate of 15 mL min⁻¹.

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