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Removal of chromium (VI) from aqueous solution by using *Citrus limetta* Peel as an adsorbent

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ABSTRACT

Chromium (VI) is a toxic metal, which is carcinogenic in nature as reported earlier. The Citrus limetta is the family of citrus fruits which is used as an adsorbent in this study. The removal efficiency of chromium (VI) by the Citrus limetta (CL) peel was determined by means of adsorption parameters pH, contact time, initial concentration and adsorbent dosage. From the experimental results, the equilibrium time was found to be 30 minutes for all initial concentration, the percentage removal was found to be maximum in 3g and optimum pH was 2.0. The study was visualized by the most pronounced isotherm models viz., Langmuir and Freundlich isotherm models. The data obtained was best fitted to the Langmuir and Freundlich models. This study was also extended to fit the results with kinetic models viz., pseudo first and pseudo second models. The data obtained were best fit with pseudo second order model with the high degree of correlation coefficient.

Keywords: Citrus limetta, Adsorption parameters, Adsorption isotherm, Adsorption kinetics

INTRODUCTION

Heavy metals play an important role in water pollution. The heavy metals are continuously released into the aquatic eco system from industrial process like mining, ore processing, metal processing, metal polishing, cleaning, paint manufacturing and battery manufacturing industries. These industries are producing large amounts of effluents, which are leading to detrimental effects on human life and environment, when it is discharged into water bodies. Moreover the heavy metals are not metabolized and they are bioaccumulated into our body through the biological chain [1]. The major pollutants in effluents are mercury, chromium, arsenic, lead, zinc, copper, and cadmium. Among them chromium is one of the most toxic metal which causes serious health hazards to the environment. Chromium is the second most common inorganic contaminant in the ground water. Chromium is the 21st most abundant element in Earth's crust with an average concentration of 100 ppm. Large numbers of important alloys contain chromium as the principle element. Chromium has broad industrial applications, such as alloy industries, paper and pulp, basic steel works foundries, petroleum refining industries, mining, dyes and pigments, textile, leather, tanning and electroplating. Generally chromium exists in two oxidation state they are Cr(III) and Cr(IV) [2]. Although trivalent chromium (Cr(III)) is required in trace amounts for sugar and lipidmetabolism, few cases have been reported where its complete removal from the diet has caused chromium deficiency. Chromium (VI) is one such metal, which is a potent carcinogenic and mutagenic[3]. Also asthma, bronchitis, ulceration and perforation, liver and kidney damages are caused due to the airborne exposure of Cr(VI) to the workers [4]. Chromium (VI) is becoming more toxic form of the metal due to its association with oxygen as chromate (CrO_4^{2-}) ions. It is a strong

oxidizing agent and in the presence of organic matter, it is reduced to chromium (III), more rapidly, in acidic environment. However, at high concentration, chromium (VI) may overcome the reducing capacity of environment and thus, persists as a pollutant. Its concentration in industrial waste water ranges from 0.5 mg/L to 270 mg/L [5]. According to that of Environment protection agency (EPA) the tolerance limit for the discharge of Cr (VI) into inland surface water is 0.1 mg/L and in potable water is 0.05 mg/L. The Cr (VI) is considered as a pollutant by Environment protection agency (EPA) because of its toxicity, water soluble and carcinogenic nature [6]. The permissible limit for chromium based on World Health Organization (WHO) value is 0.05 mg/l and it is also referred as carcinogenic and genotoxic [7]. The Bureau Indian Standard (BIS) given that the no relaxation beyond 0.05 mg/l for portable water above this limit may cause carcinogenic [8]. According to the ministry of environment and forest, India suggests that the minimal national standard (MINAS) has a limit to discharge the effluent in surface water as 0.1 mg/l [9]. The LD₅₀values for chromium (VI) ranged between 50 and 150 mg/kg [10].

So it is necessary to remove such a toxic metal from our environment. In practice there are various conventional methods available for the removal of toxic metals such as reverse osmosis, precipitation, chemical reduction etc., but these methods are required high experimental set-up, more expensive and also less effective. Of these methods biosorption is the most promising method for the removal of toxic metals which is low cost, produced less secondary sludge, more effective and eco-friendly. Biosorption is important from two points that the elimination of poisonous metals and the recovery of precious elements. Generally biosorption is considered to be fast physico-chemical method and it may possible when the dissolved species present in sorbent and sorbate to be sorbed with aid of the higher affinity of biosorbent species for the sorbate species [11]. In recent years, many researchers used an agricultural waste such as fruit peels [12, 13], plant leaves [14, 15] vegetable shells [16, 17, 18, 19], rice husks [20] and sawdust [21, 22] etc. for the adsorption process because of their high removal efficiency and low cost. In this study, *Citrus limetta* peel was taken as an adsorbent for the removal of the chromium (VI). The present study investigates the removal efficiency of a *Citrus limetta* peel against hexavalent chromium, analyzes the adsorption parameter and the experimental results are also employed to adsorption isotherm and kinetics.

MATERIALS AND METHODS

Adsorbent:

The *Citrus limetta* fruits were collected in the local market. The collected fruits were peel off and the peel was taken as an adsorbent for this experimental work. The peel was washed with distilled water till the adhering dirt removed. Then the peel was dried in the air oven. The dried peel was grinded to fine particles and sieved into 0.5 mm. The sieved adsorbent was stored in an air-tight container. No other chemical modification was taken place.

Adsorbate:

The stock solution (100 mg/l) was prepared by dissolving 0.283 g of $K_2Cr_2O_7$ (AR grade, Merck chemicals) in distilled water. The working solution was obtained by diluting stock solution. Once again the concentration of stock and working solutions were confirmed by calorimeter.

Batch adsorption studies:

The batch adsorption studies were carried out to determine effect of pH (2-9), contact time (10-60), initial concentration (15-65 mg/l) and adsorbent dosage (1-3g). 100 ml of working solution was taken in the 250 ml conical flask stirred till the equilibrium was attained. The pH of the working solution was adjusted using 0.1M HCl and 0.1M NaOH. The biosorbed solution was taken at the pre-set time interval and the solutions were filtered through whatmann 42 paper. The concentration of chromium (VI) solution was analyzed by calorimeter at 540 nm using diphenyl carbazide as the reagent. Each experiment was done triplicate to ensure the concordant values. The percentage removal and amount adsorbed were calculated using the following relationship

$$\% Removal = \frac{C_0 - C_e}{100}$$

Where C_o is the initial concentration of sorbate solution in (mg/l) and the C_e is the concentration of the sorbate solution at equilibrium, (mg/l).

Amount of sorbate adsorbed by the sorbent solution at the equilibrium time was calculated by the following formula

$$q_e = \frac{(C_0 - C_e)}{M} * V$$

Where q_e is the amount adsorbed by the sorbent at the equilibrium time, (mg/g), C_o is the initial concentration of sorbate (mg/l) and C_e is concentration of sorbate at the equilibrium, (mg/l), V is the volume of the sorbate solution, (ml) and M is the mass of the sorbent, (g).

The kinetic studies were conducted as same that of the equilibrium studies. The residual sorbate solution was collected at the set of time intervals. The qt (mg/g) amount adsorbed at any time t. min, were calculated by the following equation

$$q_t = \frac{(C_0 - C_t)}{M} * V$$

Where C_o is the initial concentration of the sorbate solution, (mg/l), and C_t is the concentration of the sorbate solution at any time, t. (min), V is the volume of the sorbate solution, (ml) and M is the mass of the sorbent, (g).

Equipment:

The pH of the working solution throughout the experiment was measured by using Elico-Perkin Elmer 138 water quality analyzer. The concentration of the solution was calculated by the aid of Photo-Colorimeter AE 11D and functional group present in the surface of the adsorbent were determined by FT-IR.

RESULTS AND DISCUSSION

Structural elucidation of the adsorbent: FT-IR analysis of the adsorbent:



Fig.1 FT-IR pattern for pure sorbent before adsorption. Particle size = 0.5 mm

The FT-IR spectra of pure and adsorbed sorbent are shown in the fig.1 and fig.2. The pure sorbent composed of many peaks which is the characteristics of functional groups present in the surface. From fig.1, the intense, broad peak present in the region of 3458 cm⁻¹ is due to the stretching of–OH and –NH indicates that presence of hydroxyl and amine groups in the surface. The weak, broad peak at 2929.45 cm⁻¹ and 2863.03 cm⁻¹ is the characteristics of – CH stretching indicates the presence of methyl group. The medium, intense peak at 2382.19 cm⁻¹, the sharp, intense peak at 2357.11 cm⁻¹ and the medium, broad peak at 2307.93 cm⁻¹ due to the C=N stretching indicates that the presence of aritiles group in the surface. The weak peak at 1740.83 cm⁻¹ due to the C=O stretching indicates that the presence of carboxylic acids or esters. The weak peak at 1625.10 cm⁻¹ due to C=O stretching indicates that the presence of amide I band. The weak peak at 1518.04 cm⁻¹ due to N-H bending indicates that the presence of alkyl halide in

the surface of the adsorbent. The FT-IR spectrum of adsorbed sorbent (fig.2) has the noticeable shift in the corresponding peaks at 3443.08 cm⁻¹, 2301.48 cm⁻¹, 1508.40 cm⁻¹ and 669.33 cm⁻¹. This implies that the -OH, -NH, -C=N, -R-NH and Al-X groups are responsible for the favourable adsorption of hexavalent chromium onto the CL biomass.



Fig.2 FT-IR pattern for the adosrbed sorbent dose after adsorption.

Table 1 FT-IR spectra for the pure and adsorbed sorbent

ID Spectre		Eurotional group		
IK Specifia	pure sorbent	Adsorbed sorbent	Interference	Functional group
1	3458.52	3443.08	-15.44	-OH and -NH
2	2307.93	2301.48	-06.53	Nitriles
3	1518.04	1508.40	-09.64	Amides
4	0680.90	0669.33	-11.34	Halides

Effect of pH



Fig.3 Effect of pH on the removal of Cr (VI) by sorbent at room temperature Conditions: Adsorbent dosage = 1.5g; Adsorbate conc. = 25 mg/l; Contact time = 30 min

pH is the controlling parameter of the adsorption process [23]. The change in pH affects the solubility of metal ions, functional groups and surface charge of the adsorbent. The effect of the pH was studied by varying the pH from 2 to 9 while keeping other parameters constant. Fig.3 shows that the maximum percentage removal occurs at pH 2. Our results were well accompanied with the previous work [24, 25]. The percentage removal was high at acidic pH and it becomes low when we move down to the basic pH. This is because at acidic pH, it is well known that the anionic forms of dichromate ions are $CrO_4^{2^\circ}$, HCrO₄⁻ and CrO_7^{-} . Moreover at acidic pH, surface of the sorbent gets

protonated that result in strong electrostatic attraction between cations and anions. At basic pH the overall charge of surface of the adsorbent become negative i.e., the surface of the sorbent become deprotonated that results in dual competition between the both anions. So that the uptake of sorbate by sorbent becomes insignificant in basic pH.

Effect of Adsorbent Dosage:



Fig.4 Effect of adsorbent dosage on the removal of Cr (VI) by the sorbent at room temperature Conditions : Adsorbent dosage = 1-3g; Adsorbate conc. = 25-65 mg/l; Contact time = 30 min; pH = 2.0

The adsorbent dosage is an incredible factor which determines the sorbent-sorbate equilibrium of the system and also it is essential when consider the effective metal sorption of the system. In this study, the adsorption of Cr(VI) on the CL biomass observed by varying the dosage of CL from 1g to 3g with various initial concentration of Cr(VI) solution from 25 mg/l to 65 mg/l while keep the other parameters constant. The figure 4 shows that the percentage removal was increased when we increases the dosage and decreases with the increase of initial concentration. The maximum percentage removal was observed at 3g. This is because the availability of binding sites and surface area were becoming more and more when increasing the dosage.

Effect of Contact time with Initial concentration:



removal by the sorbent

Fig.6 Adsorption capacities of various time on the removal of Cr (VI) by the sorbent

These studies were done at various initial concentrations from 25 mg/l to 65 mg/l with the contact time (10-60 min) and keep other parameters constant. From the figure 5 the percentage removal was increase with the contact time (10-60 min) at certain time it reaches maximum. For all the initial concentrations, the equilibrium attained at 30

minutes. It also clear that the uptake of adsorbate by the sorbent was quick at the initial stages but slow down until reaches equilibrium. But after that there was no favorable sorption takes place. These conclude that the adsorption process towards the metal binding was spontaneous. From the fig.6 we come to know that the amount adsorbed at the equilibrium time was increased from 1.6 to 3.9 mg/g when we increase the initial concentration from 25 mg/l to 65 mg/l. Thus the initial concentration is an important driving force to overcome all mass transfer resistances of the Cr(VI) between aqueous and solid phase.

Adsorption Isotherm

Generally adsorption isotherm is used to attribute the distribution and interactions between the solid-liquid system and optimizing the use of adsorbents [26]. It also gives the equilibrium relationship between adsorbent and adsorbate. Our experimental data obtained were fitted into most pronounced isotherm model for their acceptability.

Langmuir Isotherm:

Langmuir isotherm provides information about homogeneity of the system which also gives the additional idea about the monolayer surface coverage, availability of adsorption sites and ensures no interaction between the adsorbed molecules [27]. It also indicates that all the adsorption sites are have equal affinities and adsorbed molecules are independent to each other i.e., uptake of first one does not affect the sorption capacity of other [28]. The linear form of Langmuir isotherm equation is represented as:

$$\frac{C_e}{q_e} = \frac{1}{bQ_0} + \frac{C_e}{Q_0}$$

Where, C_e – equilibrium concentration (mg/l) q_e – amount adsorbed (mg/g) Q_0 = maximum monolayer adsorption capacity per unit weight b = affinity of the adsorption sites.



Fig. 7 Langmuir isotherm model for Cr (VI) by sorbent at room temperature Conditions: Adsorbent dosage = 2.0g: Adsorbate conc. = 15-65 mg/l; Contact time = 30 min; pH = 2.0

Fig.7 show that the Linear plot of C_e/q_e vs qe. The Q_0 and b are calculated from the slope and intercept of the linear plot. The acceptability of the Langmuir isotherm is represented by the dimensionless factor R_L ,

$$R_L = \frac{1}{1 + bC_0}$$

 C_0 = initial concentration (mg/l), the R_L value between the 0 and 1 indicates that the favorable adsorption.

From table 2 the values of R_L of all the initial concentrations were found to be between 0 and 1 and also R_L decreases with the increase of initial concentration. This shows that the adsorption of chromium on the CL is favourable. The Q_0 and b values obtained from the experiment are 4.16 and 12.93 respectively. Thus Q_0 indicates that the maximum adsorption corresponds to saturated monolayer with constant energy and no transmission was

occurred on the surface of adsorbent and also the correlation coefficient R^2 value was found to be 0.9878 shows the applicability of Langmuir isotherm.

Initial Concentration	Dimensionless Factor
(Mg/l)	(R _L)
25	0.0030
35	0.0022
45	0.0017
55	0.0014
65	0.0011

Table 2 Dimensionless factor for all Initial Concentrations

Freundlich Isotherm:

The Freundlich isotherm is applicable to both monolayer (chemisorption) and multilayer adsorption (physisorption) and it is based on the assumption that the adsorbate adsorbs onto the heterogeneous surface of an adsorbent [29]. This also assumes that the adsorption energy of the metal adsorbed onto the adsorption sites on adsorbent depend or independent to the adjacent sites. It does not give any information about the surface saturation. The Freundlich model is given by the following equation,

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$

Where q_e = amount of adsorption, k_f = sorption capacity 1/n = intensity of adsorption.



Fig. 8 Freundlich isotherm model for Cr (VI) by sorbent at room temperature Conditions: Adsorbent dosage = 2.0g; Adsorbate conc. = 15-65 mg/l; Contact time = 30 min; pH = 2.0

Table : 3 Langmuir and Freundlich parameters for the uptake of Cr (VI) by sorbent CL

	Langmuir parameter		Correlation coefficient (\mathbf{P}^2)	
Langmuir isotherm	Q _o (mg/g	b (l/mg)	Correlation coefficient (K)	
	4.16	12.93	0.9878	
	Freundlich parameter		Correlation coefficient (\mathbf{P}^2)	
Freundlich isotherm	K _f	1/n	Correlation coefficient (K)	
	1.724	0.481	0.9941	

Fig.8shows that the linear plot log q_e vs log C_e . From this, Freundlich constants k_f and b can be obtained. The constants k_f and b represents the curvature and steepness of the isotherm. Generally the 1/n value lie between 0 and 1 is a measure of surface heterogeneity, it becomes more heterogeneity, the value proceeds very closer to zero. In this study n value was greater than unity indicating chemisorption. An isotherm with n>1 was classified as L-type isotherms reflecting a high affinity between adsorbate and adsorbent and indicative of chemisorption [29]. The values of Freundlich constants k_f and 1/n were found to be 1.7241 and 0.481. The n value obtained from the

experiment in between 1 and 10. This indicates that the adsorption of chromium onto the CL was favourable adsorption [30]. The R^2 value of Freundlich isotherm was 0.9941 obtained from the regression analysis. Thus the CL biomass exhibits both Langmuir and Freundlich isotherm. This indicates that the sorption process is complex, which follows more than one mechanism [1].

Adsorption kinetics:

Kinetic models are obviously used to predict the rate and mechanism of the adsorption process in which we ascertain the factor like physical or chemical adsorption, nature of the adsorbent, ambient temperature, pH of the solution, influence the rate and mechanism of the adsorption process [32]. The experimental results are interpreted to the most pronounced kinetic models viz., pseudo first order and pseudo second order for their applicability.

Pseudo-first order kinetics:

To explain the pseudo-first kinetics the legergren equation is widely used. This equation considered the rate of ionexchange adsorption in the exchange of metal ions from aqueous solution by the solid. Thus the equation simply implies that the sorption capacity of the solid. The legergren equation is represented as follows [33].

$$\frac{dq_t}{dt} = k_1(q_e - q_t)...(1)$$

Integrating the equation for the boundary conditions t = 0 to 1 and $q_t = 0$ to q_t gives rise to the linear form as shown in equation (2)

 $\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}....(2)$

Where k_1 is the rate constant of the pseudo-first order equation (1/min), q_e is the amount adsorbed by the sorbate in (mg/g), q_t is the amount adsorbed by the sorbate in time t in (mg/g).



Fig.9 Pseudo-first order kinetic model for the removal of Cr (VI) by the sorbent at room temperature *conditions: Adsorbent dosage* = 1.5*g*; *Adsorbate conc.* = 25-65 *mg/l; Contact time* = 1 *hr;* pH = 2.0

The rate constant k_1 and $q_{e(cal)}$ was determined by the slope of linear plot $log(q_e-q_t)$ vs time t as shown in the fig.9. $q_{e(cal)}$ obtained from the linear plotwas correlated to that of the $q_{e(exp)}$ values. The difference between them was much large. Moreover the correlation coefficient R^2 values were closeto linear on lower initial concentration but we move down the higher concentration R^2 values far away to linearity. This was because the sorption was not occurred only ion-exchange mechanism but other sorption mechanisms were also occurring. Pseudo-first order was not well fit over range of contact time in most cases reported [34].

Table	4
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		Pseudo-first order			
Initial	$qe_{exp}(mg/g)$	$qe_{cal}(mg/g)$	K1	\mathbb{R}^2	
Concentration (mg/l)					
25	1.60	0.0017	0.0154	0.9838	
35	2.20	0.0381	0.0165	0.9522	
45	2.76	0.2608	0.0304	0.941	
55	3.36	0.3385	0.0321	0.9136	
65	3.90	0.0080	0.0035	0.3956	

Pseudo second order kinetics

A pseudo-second-order equation is applied to explain how the rate depends on the sorption capacity but not the concentration of the sorbate. It is based on the sorption capacity of the solid phase. The pseudo-second order model is developed on the prediction that chemisorption is the operative reaction mechanism. The pseudo second-order kinetics rate equation can be written as follows [35].

Separating the variables in equation (1) gives

 $\frac{dq_t}{(q_e - q_t)^2} = k_2 dt....(2)$

Integrating equation (2) for the boundary conditions t = 0 to t and $q_t = 0$ to q_t , become

 $\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t....(3)$

Hence the linear form of pseudo-order kinetics equation can be represented as follows

$$\frac{1}{q_t} = \frac{1}{k_2 q_c^2} + k_2 t....(4)$$

 k_2 is the rate constant of the pseudo-second order equation, (g/mg min), q_e is the amount adsorbed by the sorbate (mg/g) and qt is the amount adsorbed by the sorbate at time t (mg/g).



Fig. 10 Pseudo-second order kinetic model for the removal of Cr (VI) by sorbent Conditions : Adsorbent dosage = 1.5g; Adsorbent conc. = 25-65 mg/l; Contact time = 1 hr; pH = 2.0

The values of $q_e (mg/g)$ and k_2 were obtained from the linear plot of pseudo-second order model shows in the fig.10. The rate constant k_2 values were decreased with increase in initial concentration. The $q_{e(cal)}$ seems to be much closer to the $q_{e(exp)}$. In general the validity of the kinetic models was tested by the correlation coefficient R^2 . In this study correlation coefficient ($R^2\pm1$) values much closer to linearity. This shows that the pseudo-second order kinetic model was suitable model for the adsorption of chromium onto the CL biomass. From the experimental data, the rate

of the adsorption may be controlled by the chemisorption. Many of the earlier cases suggest that the pseudo-second order model was the suitable model for the adsorption [36, 37, 38].

Initial	aa (maa/a)	Pseudo-second order		
Concentration (mg/l)	qe _{exp} (mg/g)	qe _{cal} (mg/g)	K ₂	\mathbb{R}^2
25	1.60	1.61	3.45	0.9999
35	2.20	2.22	2.98	0.9999
45	2.76	2.77	2.37	0.9999
55	3.36	3.44	1.96	1.0000
65	3 90	4 00	1.86	1 0000

Та	ble	5
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## Goodness of the kinetic model:

The best fitness of the kinetic models are optimizing with tool of chi-square test. This is nothing but an error analyzing test for the suitability of the kinetic models. The chi-square test carried by the sum of the square differences between the experimental data and calculated data. The equivalent mathematical statement is:

$$x^{2} = \sum \frac{(q_{e(exp)} - q_{e(cal)})^{2}}{q_{e(cal)}}$$

Where  $q_{e(cal)}$  (mg/g) is the amount adsorbed by the adsorbent is calculating from the model and  $q_{e(exp)}$  is the amount adsorbed by the adsorbent from experimental data.

From this equation we can calculate the chi-square value. For instance the  $q_{e(exp)}$  is similar to the  $q_{e(cal)}$ ,  $\chi^2$  will be small if the  $q_{e(exp)}$  is differ from the  $q_{e(cal)}$ ,  $\chi^2$  will be large. If  $\chi^2$  value is large, the model is not suitable, if  $\chi^2$  value is small, the model is said to be a suitable model. Thus the non-linear chi-square test is used to confirm the absolute model of the system.

In the present study, set of data was fitted into the chi-square equation. Here difference between the  $q_{e(cal)}$  and  $q_{e(exp)}$  of the pseudo-second order model (0.00281) were very small i.e.,  $\chi^2$  value was small confirm that the pseudo-second order model was the suitable model over the pseudo-first order model (238.6).

## CONCLUSION

In this study the *Citrus limetta* peel was found to be effective adsorbent for the removal of hexavalent chromium. 100 % removal is carried out by using 3g of adsorbent for all initial concentration and maximum removal of chromium is done at pH 2.0. From the isotherm studies, the adsorption capacity  $Q_0$  obtained from the Langmuir isotherm was found to be 4.16. Regression coefficient  $R^2$  values obtained from Langmuir and Freundlich isotherm were (0.9878) and (0.9941) indicates that the acceptability of this models. This strongly suggests that the favourable adsorption take place on the surface of the adsorbent. Thus *Citrus limetta* peel was suitable adsorbent for the removal of hexavalent chromium. From the results of the kinetic model, the pseudo-first order model had bad correlation results; this implies that pseudo-first order model is not a suitable for this system. The results of the suitable model for this system and also the suitability was also examined through the chi-square test. The chi-square value firmly suggests that the pseudo-second order model is a suitable model of this system.

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