PHYSICO-CHEMICAL AND SURFACE CHARACTERISATION OF A RENEWABLE LOW-COST BIOSORBENT FOR THE UPTAKE OF HEAVY METAL IONS FROM AQUEOUS SOLUTION

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ABSTRACT

The persistence and toxicity of heavy metals in the environment is of global concern. Powdered biomass from the stem of *Diceriocaryum eriocarpum plant* (DEP) was characterised and applied as a possible biosorbent for the uptake of Pb(II), Cu(II) and Cr(VI) from aqueous solution. The bulk density and moisture content of DEP stem were found to be 0.7026 g/mL and 5.36%, respectively. Thermogravimetric analysis showed the stability of the biosorbent up to 200°C. Results from scanning electron microscopy (SEM) showed a flasky and crack filled surface morphology. The Brunauer-Emmett Teller (BET) isotherm gave a total surface area of 2.5052 m^2/g. XRF analysis revealed the presence of calcium as the major element present. Experimental data from Fourier-Transform Infra-red spectrometer indicated the presence of hydroxyl, carbonyl, amino and nitro functional groups. The biosorbent showed 95.4%, 54.9% and 16.3% uptake efficiencies for Pb(II), Cr(VI) and Cu(II), respectively. Kinetic data for the biosorption of Pb(II) gave a Pseudo-second order as the best fitting kinetic model. The equilibrium data obtained best fitted into the Freundlich isotherm model ($R = 0.99$) than the Langmuir ($R = 0.98$) model. Powdered stem from DEP is a suitable biosorbent for the uptake of heavy metals from aqueous solution.

Keywords: biosorbent, bulk density, DEP, environment, Freundlich, heavy metals, kinetics, Langmuir, remediation, wastewater.

1 INTRODUCTION

Inadequate supply of potable water is a global problem which is exacerbated particularly in developing countries of the world. Reliance on surface water has been a welcome alternative due to population growth and increased industrialisation [1], [2]. The quality of surface water has declined as it serves as the best sink for several industrial and domestic wastes [3], [4]. Research into wastewater management has largely focused on heavy metals due to their deleterious effects and persistence once released to the environment [5], [6]. Several short and long-term effects on humans and the aquatic ecosystems are well documented [6]–[10].

The toxicity and persistence of heavy metals in various environmental media still remains a major cause of challenge despite decades of research into it [11], [12]. US EPA published 13 metals which include: Ag, As, Be, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Se, Tl and Zn as priority pollutants due to their adverse effects on plants, aquatic organisms and on human health [13], [14]. Several physiological disorders in humans and other biological systems have been linked to the consumption of metal rich water. Adequate preventive mechanisms must be put in place to deter the introduction of such metals accumulation into the environment and human food chain [12]. National and international authorities have set guidelines and threshold limits for the monitoring of these contaminants due to the health hazards brought by their presence in water and other environmental media.

The use of low-cost renewable biosorbents are preferred to the costly conventional methods and are currently undergoing rigorous research by scientists owing to their ability to sequester heavy metals at trace levels. *Dicerocaryum Eriocarpum plant* (DEP) is a

WIT Transactions on Ecology and the Environment, Vol 228, © 2018 WIT Press
www.witpress.com, ISSN 1743-3541 (on-line)
doi:10.2495/WP180301

perennial (sometimes annual), prostrate herb with long trailing stems (about 3.5 m long) that usually scramble over the ground. It is commonly found in Southern African countries on grasslands, dune slopes and river banks of high elevation (900–1200 m) [15]–[16]. This paper presents the characterisation and potential use of a renewable, low cost and environmental friendly material for the uptake of heavy metals from aqueous solutions.

2 MATERIALS AND METHODS

2.1 Preparation of the biosorbent

The plant samples were randomly collected from grasslands in Siloam village, Limpopo Province, South Africa. Identification of the plant as *Dicerocaryum eriocarpum* species of the *Pedaliaceae* family was done by botanists from Botany Department, University of Venda [17]. The plant was washed with tap water, sun dried for a day and oven dried at 105°C for 18 hours. After drying, other parts of the plant such as the leaves and root were detached from it while the stem was ground with a hammer mill and fractionated using analytical sieves. Particle size of <150 µm was chosen for all the various experiments.

2.2 Reagents

All the reagents used were of analytical grade. Merck (pty) Limited in Johannesburg, South Africa supplied the Hydrochloric acid (32%), sodium hydroxide and 1000 mg/L stock solution of Pb(II), Cu(II) and Cr(VI) used in the various experiments of this study.

2.3 Determination of bulk density, moisture content and mass of loss on ignition

The bulk density and moisture content were determined using the method reported by Moyo and Chikazaza [18]. Briefly, sufficient quantity of the biosorbent was transferred into a 10 mL measuring cylinder of 1.0 cm diameter. The bulk density was obtained by the relation in eqn (1) and was expressed in grams per milliliter.

$$\text{Bulk density (g/mL)} = \frac{W_b}{V_C}, \tag{1}$$

where W_b is the weight of biosorbent filling 10 mL measuring cylinder on gentle tapping, V_c is the volume of the cylinder.

10 g of the biosorbent was put inside oven at 105°C in order to obtain the moisture content. After 6 hours, it was removed and cooled in a desiccator to prevent re-absorption of atmospheric moisture. The percentage moisture content was calculated using eqn (2),

$$\%\, moisture\ content = \frac{(W_2 - W_3)\times 100}{(W_2 - W_1)}, \tag{2}$$

where W_1 is the weight of empty crucible, W_2 is the initial weight of the crucible with the sample, W_3 is the final weight of the crucible with the sample.

The loss of mass on ignition was performed by accurately weighing 12 g of the biosorbent into a porcelain crucible and putting it inside a furnace at a constant temperature of 600°C for 2 hours. The charred biosorbent was removed and placed in a desiccator for cooling. The difference in mass of the original and charred sample represents the mass loss on ignition.

2.4 Instrumentation

X-ray florescence measurement was carried out using Rigaku, ZSX Primus II X-ray Fluorescence spectrometer. Fourier transform infrared (FT-IR) spectrometer supplied by

Perkin Elmer was employed to identity the functional groups that are present on the biosorbent. Before analysis, a mixture of biosorbent and powdered KBr was mixed in ratio 1:20 and the mixture were pelletised [17]. Surface morphology was determined using a scanning electron microscopy (SEM). The surface area was analysed using a surface area analyzer (Micromeritics Chemisorption ASAP 2020 supplied by Norcross, USA). The thermal stability of the biosorbent was performed using a Perkin Elmer thermal analyzer (Waltham, Ma, 02451, USA) [17].

2.5 Biosorption studies

Batch experiments of the biosorption process were carried out in 100 mL polyethylene bottle with caps. Varying amount of the stock solution was added into the containers to achieve the desired concentrations. The desired pH of the solution was obtained by adjusting it using 0.1 M HCl and NaOH, respectively. Biosorbent dosage is an important parameter in any biosorption experiment as it gives a clue to the quantity of the biosorbent to be used in order to obtain an efficient uptake of the target pollutant. Initially, 1.0 g of the biosorbent was added to 10.7 mg/L of initial Pb(II), Cu(II) and Cr(VI) solutions at a pH of 6.0, shaking speed of 250 rpm and time = 60 minutes. The result showed uptake efficiencies of 95.5%, 54.9% and 16.3% for Pb(II), Cu(II) and Cr(VI), respectively. Pb(II) was chosen for subsequent biosorption studies because the biosorbent had a greater affinity for it than the other metals investigated. Different quantities of the biosorbent in the range of 0.01–2.0 g were added to 10.7 mg/L of initial Pb^{2+} under the same experimental condition (shaking speed of 250 rpm and time = 60 minutes). The optimum dosage was obtained and used for subsequent experiments.

pH plays an important role in the biosorption of metals to the surface of a biosorbent. Some metals are better adsorbed at low pH values while others at high pH and a few shows independences from the pH of the solution. A pH range of 2–14 was investigated in this experiment, while other operating parameters were kept constant. The effect of initial concentration of Pb^{2+} was investigated by varying the Pb concentrations from 1–50 mg/L.

Kinetic experiments were performed by mixing 1.0 g of the biosorbent to 40 mL of 10.7 mg/L of Pb^{2+} solution at 298 K in a 100- mL polyethylene bottle. The mixtures were then equilibrated for 60 minutes using a Stuart reciprocal mechanical shaker at 250 rpm at different time intervals. Atomic Absorption spectrophotometer supplied by Perkin Elmer was used to analyse the concentrations of heavy metals prior and after the biosorption process. The biosorption capacity was calculated by using the relation in eqn (3)

$$q_e = (C_o - C_e)V/M, \tag{3}$$

where q_e is the biosorption capacity in mg/g, C_o and C_e are the initial and equilibrium concentration of lead(II) ion in mg/L. V is the volume of the solution in litres and M is the weight of powdered stem of DEP in grams.

3 RESULTS AND DISCUSSION

3.1 Surface characteristics of the biosorbent

Fig. 1 shows the SEM micrograph of the biosorbent. The presence of a flasky structure was observed from the SEM micrograph. The XRF analysis shows that the major element present in the stem of DEP is calcium (27.8%) followed by potassium (16.5%) (Table 1). A Brunaeur-

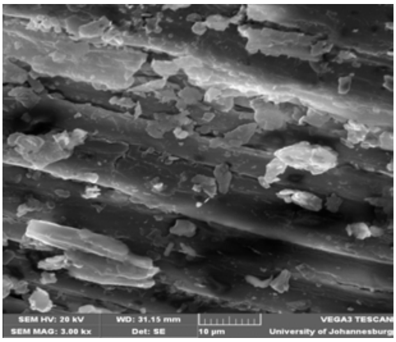


Figure 1: Surface morphology of the biosorbent.

Table 1: Chemical analysis of the biosorbent.

Component	% weight composition
Na_2O	5.92
MgO	10.5
Al_2O_3	2.55
SiO_2	7.02
SO_3	11.5
Cl	2.98
K_2O	16.5
CaO	27.8
Fe_2O_3	6.07
BaO	2.29

Emmett Teller (BET) surface area of 2.5052 m/g was obtained (Table 2) which is the range of BET values reported for other biosorbents in literature such as mucilaginous leaves of *Dicerocaryum eriocarpum*, macadamia and maize tassels with BET surface areas of 1.8517 m^2/g [17], 1.083 m/g [19] and 2.52 m/g [20], respectively. Surface area of an adsorbent usually plays a major role in adsorption experiments; generally, the larger the surface area the greater the adsorption capacity [21]. The adsorption capacity of avocado kernel seed increased when the surface area was increased by activation and carbonisation [21]. The results obtained for the bulk density and moisture contents are also presented in Table 2.

3.2 Thermal stability of the biosorbent

Thermogravimetric analysis (TGA) is used to characterise the thermal stability and decomposition of materials that occur over specific temperature ranges. Result of the TGA curve obtained is shown in Fig. 2. 8.7 mg of the dried powdered stem of DEP was heated between 30–900°C at a rate of 10°C min^{-1} using a TGA analyzer supplied by Perkin Elmer. Initially, between 30°C and 150°C the biosorbent seems to be stable with a very slight loss in weight, which could be attributed to the loss of water molecules and other volatile low molecular weight substances. A sharp increase in degradation was observed between 214°C and 390°C and this corresponds to 55.2% loss in the initial weight of the biosorbent. After

Table 2: Physicochemical characteristics of the biosorbent.

Parameter	Value
pH	5.93
Moisture content (%)	5.36
Loss of mass on ignition (%)	90
Bulk density (g/mL)	0.7026
BET surface area (m^2/g)	2.5052
Pore volume $P/P_o = 0.995$ (cm^3/g)	0.009255

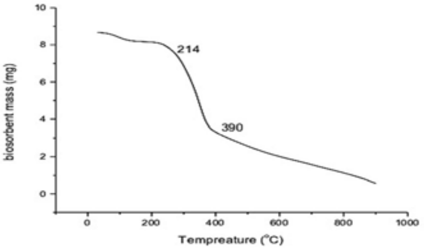


Figure 2: TGA spectra of the biosorbent.

390°C a uniform deterioration of the organic matter was recorded to 900°C. Similar thermal degradation profiles have been reported for maize tassels and vemicompost [2], [11], [22].

3.3 Functional groups analysis of the biosorbent

Fourier transform Infra-red spectroscopy was used to analyse the presence of some functional groups on the surface of the biosorbent (Fig. 3). These groups are the binding sites of the biosorbent with metallic species [22]. The peak observed at 3414 cm^{-1} is characteristic of the stretching vibrations of -N-H of primary and secondary amine and amide and -O-H of hydrogen bonded to phenols or alcohols [22]. The strong and sharp peak at 2919 cm^{-1} is due to -C-H stretching vibration of aliphatic groups [23]. The peaks at 2154 cm^{-1} and 1739 cm^{-1} are due to -C≡C- stretch of alkynes [24] and -C=O stretch of aldehydes and aliphatic esters, respectively [2]. The peaks observed at 614 cm^{-1} and 1626 cm^{-1} can both be attributed to bending vibrations of alkynes (-C≡C-H) [24] and primary amines (-N-H) [21]. The peaks observed at 1502 cm^{-1}, 1446 cm^{-1}, are due to -C=C stretch of an aromatic compound [25], while 1266 cm^{-1} and 1064 cm^{-1} can be assigned to -C-N stretch of aromatic amines [26] and -C-O stretch of alcohols, carboxylic acids and esters [21]. The presence of acidic functional groups has been implicated as the basis for metal uptake [27].

3.4 Effects of varying of operating parameters

Fig. 4 shows the effect of changes in pH values on the biosorption of Pb^{2+}. The pH of a solution is a very important operating parameter because it affects metal-biosorbent interaction, solubility of metal ions and the charge of the functional groups of the biosorbent [11], [25]. In this study, the pH was varied from 2–12. There was an inverse relationship

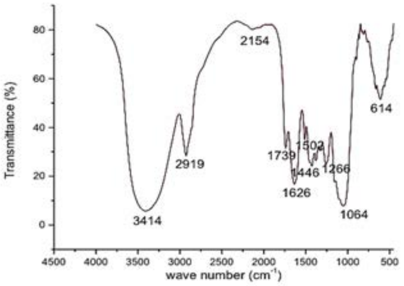


Figure 3: FT-IR Spectra of the biosorbent.

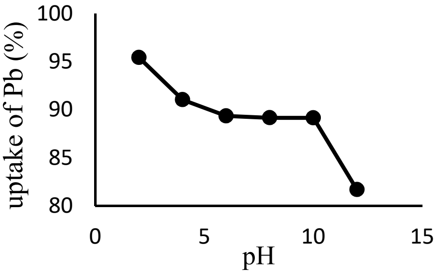


Figure 4: Variation of the uptake of Pb(II) ion with change in pH value (initial concentration=10.7 mg/L, contact time = 60 mins, T= 298 K, shaking speed = 250 rpm, biosorbent dosage = 1.0 g).

between pH and uptake efficiency i.e. as the pH increased the biosorbent ability to remove Pb(II) from aqueous solution decreased. Acidic pH is suitable for the biosorption of Pb (II) ions as the likelihood of precipitation is not expected. pH values above 4 could cause lead(II) ions to precipitate out of solution as insoluble particle. The pH value of 2 was chosen as the optimum pH for this study and further experiments were conducted at this pH value. Gupta et al. [28] reported similar optimum pH of 2 in the biosorption of chromium(VI) from aqueous solutions by green algae spirogyra species. Azouaoau et al. [29] also reported an optimum pH value in the range of 3–4.6 for the adsorption of Pb(II) from aqueous solution unto untreated orange barks. An inverse trend was, however, observed for the removal of Pb(II) from aqueous solution using activated carbon from waste biomass [30].

From Fig. 5, the biosorption capacity increased and reached equilibrium at 45 minutes. Initially there was a rapid uptake of Pb^{2+} within the first 5 minutes removing up to 95% of Pb(II) ion from a 10.7 mg/L initial concentration. This could be due to the availability of binding sites on the surface of the biosorbent. There was a slow additional uptake of the metal ion after 5 minutes up to 45 minutes accounting for 96.78% Pb removal. Afterwards, there was a slight decrease in the biosorption process, which subsequently led to a plateau indicating that equilibrium had been achieved. Patnukao et al. [31] and Ugwekar and Lakhawat [32] reported 45 minutes as the optimum time for the adsorption of Cu^{2+} and Pb^{2+} and heavy metals on activated carbon from *Eucalyptus camaldulensis dehn.* bark and peanut shells, respectively. Oluyemi et al. [33] also reported an optimum time of 45 and 50 minutes for the adsorption of Cd^{2+} and Pb^{2+} from wastewater using palm kernel shell charcoal.

There was a steady increase in the uptake of Pb^{2+} as the biosorbent dosage increased until equilibrium was established (Fig. 6) [17]. Initially, there was an increase in Pb(II) uptake from 7.6% to 30.24% when the dosage was increased from 0.05 g to 0.1 g. 91.97% Pb(II) removal was observed when 1.0 g of the biosorbent was used. This was due to increase in surface area and binding sites for the attachment of the metal ion. But when 2.0 g of the biosorbent was used, there was a slight decrease to 91.67, showing that the biosorbent was saturated at this point. This could be due to the overlapping of the adsorption sites as dosage increased [17], [20].

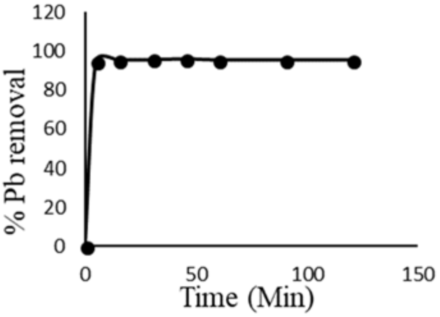


Figure 5: Variation of the uptake of Pb(II) ion with contact time (initial concentration = 10.7 mg/L, T = 298 K, pH = 2, shaking speed = 250 rpm, biosorbent dosage = 1.0 g).

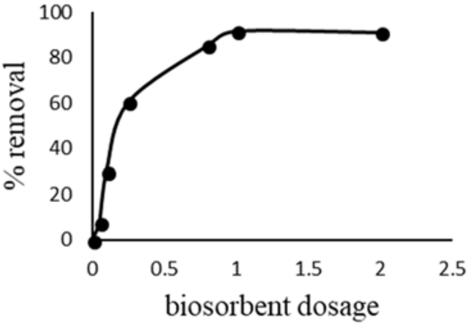


Figure 6: Variation of the uptake of Pb(II) ion with biosorbent dosage (initial concentration = 10.7 mg/L, contact time = 60 minutes, T = 298 K, pH= 2, shaking speed = 250 rpm).

3.5 Biosorption isotherms and kinetics

3.5.1 Biosorption isotherms

The experimental data obtained were analysed using the Langmuir and Freundlich adsorption isotherms. The linearised form of the models can be represented by eqns (4) and (5), respectively [34]–[36].

$$\frac{1}{q_e}=\frac{1}{q_{\max}}+\left(\frac{1}{bq_{\max}}\right)\frac{1}{C_e}, \tag{4}$$

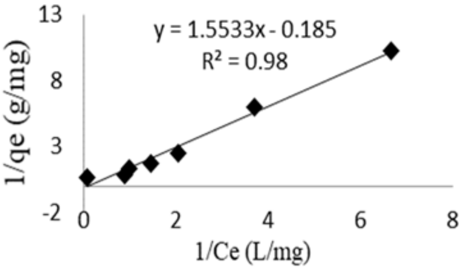
where C_e is the equilibrium concentration of the metal ion (mg/L), q_e is the quantity of Pb(II) ion adsorbed (mg/g), $q_m = q_e$ for a complete monolayer (mg/g) and b is the adsorption equilibrium constant (L/mg) [17].

$$\log q_e = \log K_f + \frac{1}{n}\log C_e, \tag{5}$$

where K_f is the adsorption capacity (mg/g)(L/mg)$^{(1/n)}$ and 1/n is the intensity of the adsorption showing the heterogeneity of the adsorbent site and the energy of distribution [17], [36].

A linear graph was obtained by plotting $1/q_e$ against $1/C_e$ (Fig. 7) and $1/q_{max}$ was the intercept with $1/bq_{max}$ as the slope. A regression coefficient of 0.98 was obtained suggesting that the adsorption conforms to Langmuir model. The equilibrium data were also fitted to the Freundlich isotherm model by plotting $logq_e$ against $logC_e$ (Fig. 8). A linear graph was obtained with a regression coefficient of 0.99 which is higher than that obtained from the Langmuir model.

Based on the correlation coefficients obtained, the Freundlich model was the most suitable to describe the adsorption process and it suggests that adsorption of Pb^{2+} onto Mucilaginous stem of DEP is through a weak intermolecular Van der Waal forces and hence a physisorption process.



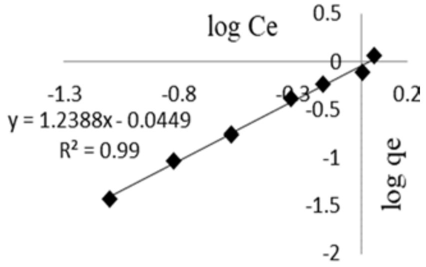


Figure 7: Langmuir plot for Pb^{2+} biosorption onto the stem of DEP.

Figure 8: Freundlich plot for Pb^{2+} biosorption onto the stem of DEP.

3.5.2 Kinetic models

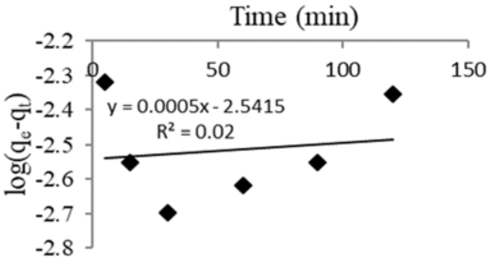
The pseudo first and pseudo second order kinetics equations were used to analyse the experimental data obtained from the influence of contact time on the biosorption of Pb^{2+} onto the powdered stem of DEP. The linearised equations for the pseudo first order and pseudo second order kinetics are presented in eqns (6) and (7), respectively [37], [38].

$$log(q_e - q_t) = logq_e - (\frac{k_1 t}{2.303}) \tag{6}$$

$$\frac{t}{q_t} = (\frac{1}{k_2 q_e^2}) = \frac{t}{q_e}, \tag{7}$$

where q_e and q_t are the amounts of Pb^{2+} adsorbed at equilibrium and at a given time t; k_1 and k_2 are the rate constants of pseudo first and pseudo second order models.

The pseudo first order plot as shown in Fig. 9 gave a poor plot with a regression coefficient of 0.02. This was not suitable to explain the kinetics of the reaction. Fig. 10 shows the graphical representation of the pseudo second order plot, which yielded a very good plot with regression coefficient of 1.0. The pseudo second order kinetics best described the kinetics of the reaction. The constants obtained from the plots are presented in Table 3.



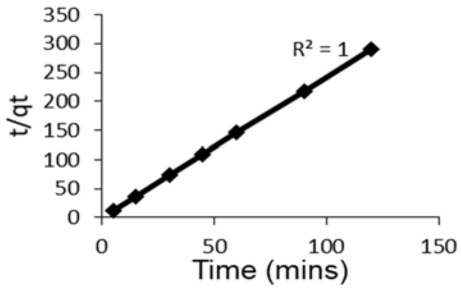


Figure 9: Pseudo first order kinetics for lead(II) ion biosorption onto the leaves of DEP.

Figure 10: Pseudo second order kinetics for lead(II) ion biosorption onto the leaves of DEP.

Table 3: Kinetic parameters for the biosorption of Pb(II) ion onto powdered stem of DEP.

Kinetic model	Parameter	Value
Psuedo-first order	q_e(mg/g)	2.87 x10^{-3}
	K_1(min^{-1})	–1.15 x 10^{-3}
	R	0.0199
Pseudo-second order	q_e (mg/g)	0.640
	K_2 (g/mg/min)	31.610
	R	1.000

4 CONCLUSION

Powdered biomass of a renewable low-cost adsorbent (stem of DEP) was characterised and its potential was explored for heavy metals uptake from aqueous solution. The adsorbent has more affinity for Pb(II) when compared to the other metals and the uptake affinity followed the trend: Pb(II) > Cr(VI) > Cu(II). Further investigation on the adsorption of Pb(II) showed an initial rapid uptake by the adsorbent which decreases while approaching equilibrium. The experimental data fitted well into the Langmuir and Freundlich adsorption isotherms but the Freundlich isotherm model best describes the adsorption process while the pseudo-second order kinetics best described the kinetics of the reaction.

ACKNOWLEDGEMENT

This study was funded by the Research and Publications committee (RPC) of the University of Venda.

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