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CONTENTS

Sorption of 2,4-dinitroanisole (DNAN) on lignin

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Abstract

The present study describes the use of two commercially available lignins, namely, alkali and organosolv lignin, for the removal of 2,4-dinitroanisole (DNAN), a chemical widely used by the military and the dye industry, from water. Sorption of DNAN on both lignins reached equilibrium within 10 hr and followed pseudo second-order kinetics with sorption being faster with alkali than with organosolv lignin, i.e. k_2 10.3 and 0.3 g/(mg·hr), respectively. In a separate study we investigated sorption of DNAN between 10 and 40°C and found that the removal of DNAN by organosolv lignin increased from 0.8 to 7.5 mg/g but reduced slightly from 8.5 to 7.6 mg/g in the case of alkali lignin. Sorption isotherms for either alkali or organosolv lignin best fitted Freundlich equation with enthalpy of formation, ΔH^0 equaled to 14 or 80 kJ/mol. To help understand DNAN sorption mechanisms we characterized the two lignins by elemental analysis, BET nitrogen adsorption-desorption and ^{31}P NMR. Variations in elemental compositions between the two lignins indicated that alkali lignin should have more sites (O- and S-containing functionalities) for H-bonding. The BET surface area and calculated total pore volume of alkali lignin were almost 10 times greater than that of organosolv lignin suggesting that alkali lignin should provide more sites for sorption. ^{31}P NMR showed that organosolv lignin contains more phenolic –OH groups than alkali lignin, i.e., 70% and 45%, respectively. The variations in the type of OH groups between the two lignins might have affected the strength of H-bonding between DNAN and the type of lignin used.

Key words: sorption; DNAN; lignin; kinetics; isotherms.

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Introduction

2,4-Dinitroanisole (DNAN) is a versatile chemical widely used in many industrial and military applications including manufacturing of dyes (Chudgar et al., 2003) and munitions formulations. Currently, DNAN because of its insensitive properties is being considered to replace TNT (2,4,6-trinitrotoluene) in the production of munitions formulations (Platten et al., 2010). Wide manufacturing and usage of DNAN may lead to wide environmental contamination of soil and water. Reportedly DNAN is known to be toxic (Dodd and McDougal, 2001) thus necessitating its removal from affected environments.

Apart from using activated carbon (GAC) to remove DNAN from water (Boddu et al., 2009); little information is available on the removal of the chemical from water. Recently, there has been considerable interest in using renewable natural products such as lignin for the development of sustainable and cost-effective materials for water treatment (Suteu et al., 2010). Lignin (Fig. 1) is the second most abundant organic biopolymer after cellulose with annual production exceeding 70 million tons per year from wastes coming from the pulp and paper and fuel production

industries (Satheesh et al., 2009). In addition, lignin is a highly functionalized polymer possessing several important functional groups including ether linkages, aliphatic and aromatic hydroxyl groups making the polymer a model matrix for sorption (Dizhbite et al., 1999; Suteu et al., 2010).

Lignin has been used as sorbent for the removal of pyrene, phenanthrene and naphthalene (Wang et al., 2007), Brilliant Red dye (Suteu et al., 2010), Cu(II) (Merdy et al., 2002; Sciban and Klasnja, 2004; Mohan et al., 2006), Cd(II) (Demirbas, 2004; Basso et al., 2004), and Pb(II) (Lalvani et al., 1997; Srivastava et al., 1994) from contaminated waters. The main objective of the present work was to explore the effectiveness of two structurally different lignins, alkali and organosolv lignins, to remove DNAN from artificially contaminated water. The kinetic and sorption equilibria were studied to gain insight into the sorption mechanism of DNAN on lignin. In addition, lignins were characterized by elemental analysis, BET nitrogen adsorption-desorption and ^{31}P NMR to help understanding the variation in sorption capacity between the two lignins.

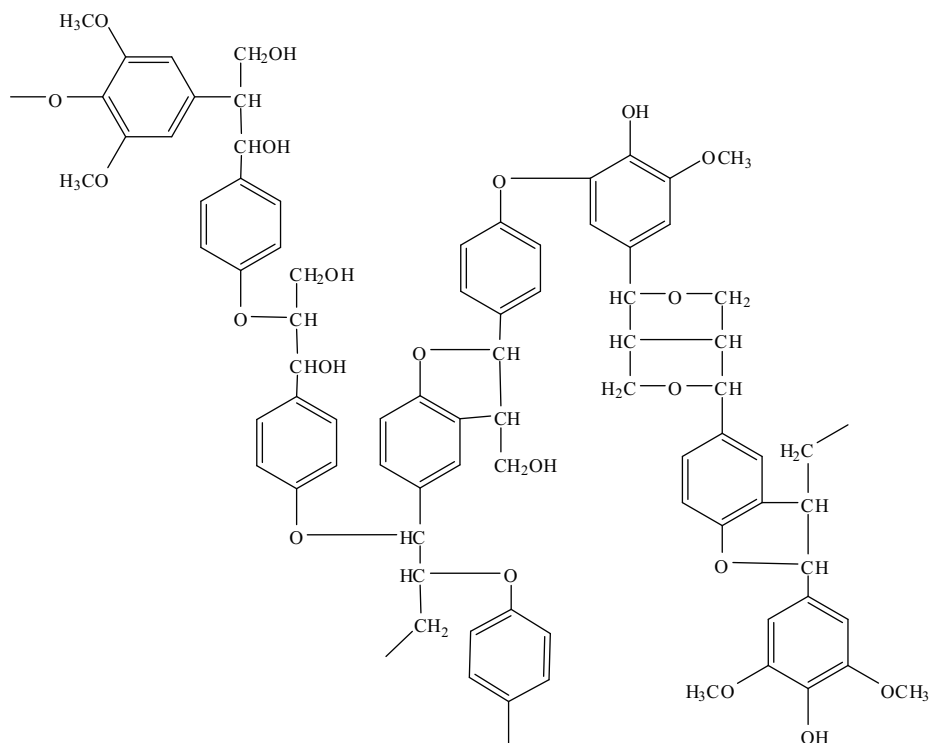* Corresponding author. E-mail: jalal.hawari@nrc.ca

Fig. 1   Chemical structure of a part of lignin polymer (Suteu et al., 2010).

1 Experimental

1.1 Materials

Both alkali and organosolv lignins were purchased from Sigma-Aldrich (Oakville, Canada) and used as received. 2,4-Dinitroanisole (DNAN) was obtained from Defense Research and Development Canada. DNAN stock solution (200 mg/L) was prepared in deionized water and working solutions (25–200 mg/L) were prepared by appropriate dilution.

1.2 Characterization of lignins

Elemental analysis was determined using Fisons instruments EAS1108. BET (Brunauer-Emmett-Teller) surface analysis was performed on a TRISTAR II 3020 surface analyzer (Micromeritics Analytical Services, USA) using the multipoint method. Lignins (5 g) were degassed at 120°C for 12 hr and nitrogen adsorption-desorption isotherms determined at 77 K. Total pore volume was evaluated from the amount of nitrogen adsorbed at P/P_0 = 0.99 (P is applied pressure, P_0 is system initial pressure). ^{31}P NMR analyses were carried out using a Bruker 500 MHz spectrometer after derivatizing lignin with a phosphotylating agent as reported previously (Akim et al., 2001; Granata and Argyropoulos, 1995). ^{31}P NMR allows the differentiation and quantification of various types of –OHs coming from the aliphatic, phenolic and carboxylic OH groups on lignin (Crestini et al., 2010).

1.3 Sorption experiments

Sorption kinetics were conducted in 20 mL borosilicate vials containing 10 mL of DNAN aqueous solution (50 mg/L) and 10 mg of either alkali and organosolv lignin.

The initial pH for alkali and organosolv lignins aqueous suspensions were 6.9 and 5.7, respectively. The tubes were stirred (250 r/min) at room temperature for 24 hr. At different time intervals, aliquots were filtered through a Millex-HV 0.45-μm syringe and analyzed for DNAN using HPLC equipped with C18 column (25 cm × 4.6 mm; 5 μm particles size) (Supelco, Oakville, Canada) and a UV detector (298 nm). The mobile phase consisted of methanol/water mixture (50%, V/V) at a flow rate of 1.0 mL/min for 15 min. All sorption experiments were conducted in triplicate. The amount of DNAN sorbed at time t, Q_t (mg/g), was calculated using Eq. (1):

$$Q_t = (C_i - C_t) \times \frac{V}{m} \tag{1}$$

where, C_i (mg/L) is the initial DNAN concentration, C_t (mg/L) is the DNAN concentration in the aqueous phase at time t, V (L) is the solution volume, and m (g) is the mass of the sorbent.

After sorption of DNAN onto either lignin was complete (aqueous concentrations stabilize), sequential desorption of DNAN from lignin was carried out using deionized water as has been described by Sheremata et al., 1999. Briefly, samples were centrifuged (3700 ×g) for 20 min and the supernatant was decanted. Then, 10 mL of deionized water were added to the remaining solid, sonicated at 20°C for 20 hr and filtered through a Millex-HV 0.45-μm syringe filter prior to HPLC analysis. This process was repeated until no DNAN is detected. The remaining lignin was then extracted with acetonitrile for subsequent analysis by HPLC to mass balance the fate of DNAN.

Sorption isotherms were obtained by determining sorption of DNAN at a temperature range 10–40°C in 20 mL borosilicate vials each containing 10 mL of DNAN

(25–200 mg/L) and 10 mg of the respective lignin. After reaching equilibrium (24 hr), the solutions were filtered through a Millex-HV 0.45-μm syringe filter and analyzed for DNAN by HPLC. The amount of DNAN adsorbed at equilibrium, Q_e, was calculated using Eq. (2):

$$Q_e = (C_i - C_e) \times \frac{V}{m} \tag{2}$$

where, C_i (mg/L) is the initial DNAN concentration, C_e (mg/L) is the DNAN concentration at equilibrium, V (L) is the solution volume, and m (g) is the mass of the sorbent.

2 Results and discussion

2.1 Sorption kinetics

Sorption of DNAN (50 mg/L) onto organosolv and alkali lignins (10 g/L) showed a biphasic process (Fig. 2), a rapid initial sorption phase followed by a much slower one. For alkali lignin, the percentage of DNAN removal increased sharply during the first 60 min during which more than 75% of the chemical sorbed then sorption increased slowly until system reached equilibrium (24 hr). For organosolv lignin the removal of DNAN reached only 40% in the first 3 hr before attaining equilibrium (24 hr). The 24 hr was considered sufficient for the significant removal of DNAN and was therefore used for all subsequent experiments.

Desorption by deionized water led to only 10% recovery of DNAN, but when acetonitrile was used, 100% of DNAN was recovered from both lignins, indicating that DNAN did not undergo irreversible chemisorption or degradation.

Data from DNAN sorption were fitted to a pseudo second-order model (Ho and McKay, 1999):

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \tag{3}$$

where, k_2 is the rate constant for the pseudo second-order kinetic equation and Q_e and Q_t are the amounts of DNAN sorbed onto lignins at equilibrium and at time t, respectively.

A plot of t/Q_t against t (Fig. 3) gives a straight line with a slope at $1/Q_e$ and an intercept of $1/k_2 Q_e^2$. The sorption capacity Q_e, rate constant k_2 and correlation coefficient,
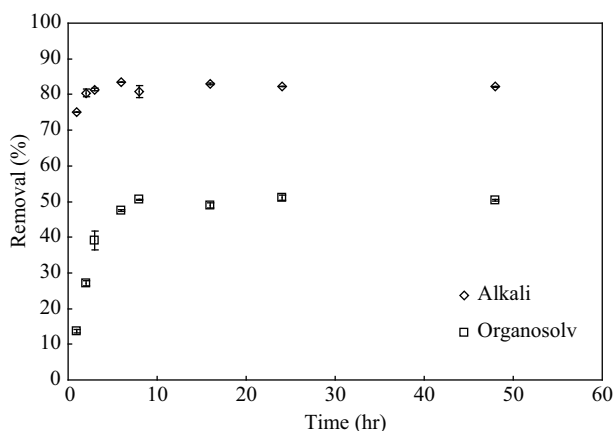
r^2, are presented in Table 1. k_2 for alkali lignin was 33 times higher than that of organosolv lignin, i.e. 10.3 and 0.3 g/(mg·hr), respectively. Rate constants obtained in this study exceeded those obtained for the sorption of DNAN onto GAC (0.07×10^{-3}–1.62×10^{-3} g/(mg·hr)) (Boddu et al., 2009). More rapid sorption on lignins might be attributed to the presence of several functional groups, e.g. –OH and –COOH, in lignin that are absent in the case of GAC.

Table 1 Pseudo second-order kinetic parameters for DNAN sorption (50 mg/L) to lignins (10 g/L)

Lignin	k_2 (g/(mg·hr))	Q_e (mg/g)	r^2
Alkali	10.3	4.19	0.999
Organosolv	0.3	2.67	0.997

2.2 Sorption isotherms

Figure 4 shows the sorption isotherms of DNAN onto both alkali and organosolv lignins at a temperature range (10, 25 and 40°C) frequently encountered in natural environments. Sorption of DNAN decreased with temperature in the case of alkali lignin (exothermic sorption) (Fig. 4a) but increased in the case of organosolv lignin (endothermic sorption) (Fig. 4b). Also the effect of temperature on DNAN uptake was more pronounced in the case of organosolv lignin. For instance, by increasing temperature from 10 to 40°C, the amount of DNAN (initial concentration 100 mg/L) sorbed by organosolv lignin increased from 0.8, to 7.5 mg/g but decreased from 8.5 to 7.6 mg/g in the case of alkali lignin.

Sorption data were fitted to both the linear equation (Eq. (4)) and the logarithmic form of Freundlich equation (Eq. (5)):

$$Q_e = K_d C_e \tag{4}$$

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

where, Q_e (mg/g) is the amount of DNAN sorbed per gram of the sorbent, C_e (mg/L) is the concentration of DNAN in water at equilibrium, K_d (L/g) is the distribution coefficient, K_f ($mg^{1-1/n}g^{-1}L^{1/n}$) is the Freundlich constant that gives a measure of the sorbent capacity and $1/n$ gives

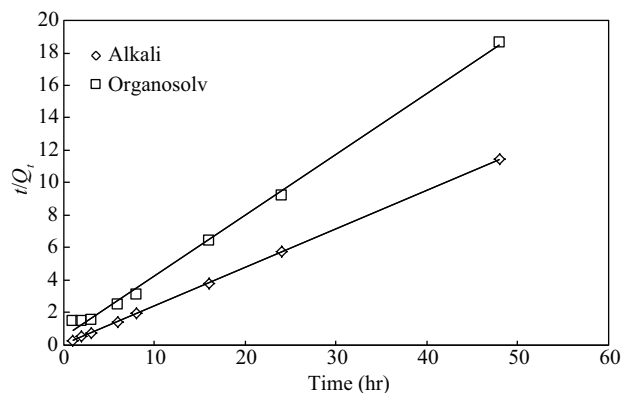**Fig. 2** Time courses for DNAN sorption (50 mg/L) onto lignins (10 g/L).

Fig. 3 Pseudo second-order kinetic model fitting for DNAN sorption (50 mg/L) onto lignins (10 g/L). Q_t is the amounts of DNAN sorbed onto lignins at time t.
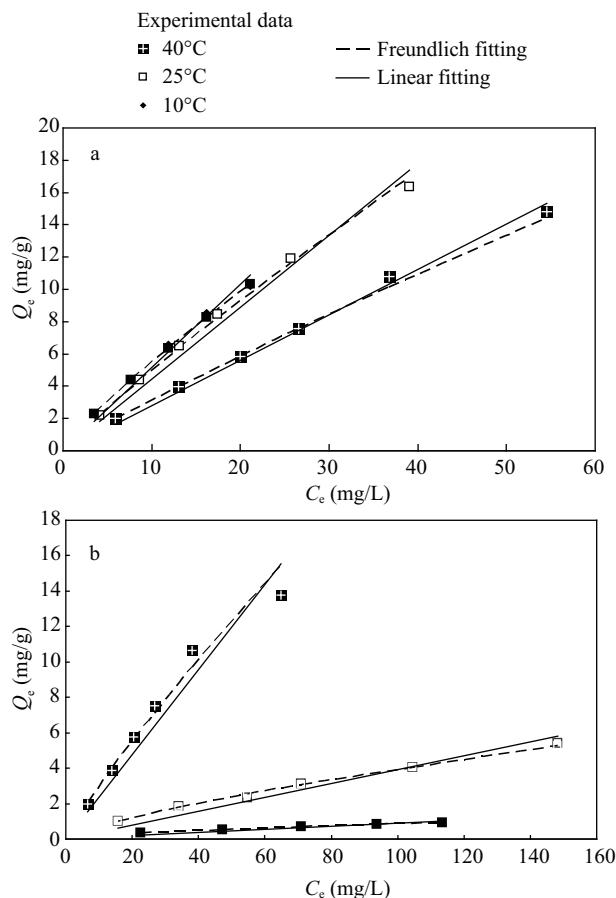
Fig. 4 Experimental and theoretical sorption isotherms of DNAN onto alkali lignin (a) and organosolv lignin (b). The standard deviations were within 5% of the corresponding values. Q_e is the amounts of DNAN sorbed onto lignins at equilibrium, and C_e is the concentration of DNAN in water at equilibrium.

a measure of the intensity of sorption. K_f and $1/n$ are represented by the intercept and the slope of the isotherm, respectively.

Sorption parameters are presented in Table 2. For both lignins, Freundlich and linear isotherms fit experimental data with r^2 higher with Freundlich isotherm than with linear one; i.e. Freundlich r^2 were 0.998 and 0.995 and linear r^2 were 0.980 and 0.942, for alkali and organosolv lignins at 298 K, respectively. The value of $1/n$ was much lower for organosolv lignin showing more non-linearity as compared to alkali lignin. Successful fitting of the experimental data with Freundlich model was attributed to the heterogeneity of lignin surface and the presence of different binding sites having different binding affinities

(Liu and Huang, 2000).

Because the value of K_f could not be used to compare different isotherms (Balakrishnan et al., 2004), instead we used K_d values to compare sorption affinity of DNAN on both lignins and to calculate sorption thermodynamic parameters. We found that K_d for alkali lignin was almost 55 and 10 times higher than organosolv lignin at 10 and 25°C, respectively, but they were comparable at 40°C (Table 2).

At the end of the sorption experiment we found that alkali and organosolv lignins were able to remove 55 and 18 mg DNAN/g lignin, respectively, as compared to 181 mg DNAN/g of activated carbon (Boddu et al., 2009). In a more recent study Zhang et al. (2011) reported the use of a modified lignin to adsorb TNT and found a maximum removal of 55.7 mg/g TNT at pH 7.

Table 2 summarizes the thermodynamic parameters obtained by plotting $\log K_d$ as function of $1/T$ using Van't Hoff equation ($\log K_d = \Delta S^0/R - \Delta H^0/RT$), where K_d (L/g) is the distribution coefficient constant and T (K) is the sorption temperature. Enthalpy of sorption (ΔH^0) of DNAN on alkali lignin was negative (–14.2 kJ/mol), i.e. endothermic but was positive (80.2 kJ/mol) in the case of organosolv lignin, i.e., exothermic. Sorption energy, ΔH^0, might also indicate the type of binding mechanism involved. ΔH^0 for alkali and organosolv lignins were 14.2 and 80.2 kJ/mol, respectively, indicating stronger sorption in the case of organoslv lignin. In support of this He et al. (2004) reported that a ΔH^0 range of 14.2 to 80.2 kJ/mol is indicative of H-bonding predominance during sorption. DNAN through its –NO$_2$ functional groups and lignin through its –OH functionalities create ideal conditions for H-bonding. ^{31}P-NMR spectroscopy of various –OH functional groups in lignin after sorption (Table 3) clearly indicates the reduction on the content of all types of –OH groups in both lignins.

Other mechanisms besides H-bonding such as π–π interactions between the aromatic rings in lignin and DNAN, dipole-dipole interactions should not be ignored.

Entropy of sorption of DNAN onto alkali lignin was negative ($\Delta S^0 = -56.4$ J/(mol·K)) indicating a decrease in the randomness at the sorbent-sorbate interface while the positive value of ΔS^0 in the case of organosolv lignin ($\Delta S^0 = 244.1$ J/(mol·K)) indicating the contrary.

2.3 Variation in sorption of DNAN by the two lignins

Elemental analyses (Table 4) showed that organosolv lignin has slightly more carbon than alkali lignin, i.e. 66.2% and 61.5%, respectively, but less oxygen 27.6%

Table 2 Freundlich and linear constants and thermodynamic parameters for DNAN sorption onto lignins

		Freundlich fitting			Linear fitting		Thermodynamic parameters	
	T (K)	K_f (mg$^{1-1/n}$g^{-1}L$^{1/n}$)	$1/n$	r^2	K_d (L/g)	r^2	ΔH^0 (kJ/mol)	ΔS^0 (J/(mol·K))
Alkali	283	0.79	0.84	0.998	0.52	0.965	–14.2	–56.4
	298	0.63	0.90	0.998	0.44	0.980		
	313	0.34	0.90	0.999	0.28	0.993		
Organosolv	283	0.05	0.61	0.997	0.01	0.752	80.2	244.1
	298	0.13	0.73	0.995	0.04	0.942		
	313	0.39	0.87	0.988	0.24	0.917		

Table 3 ^{31}P NMR quantification of different –OH types in studied lignins before and after adsorption of DNAN

	Lignin	Aliphatic-OH (mmol/g)	Phenolic-OH (mmol/g)	Carboxylic-OH (mmol/g)	Total-OH (mmol/g)
Alkali	Before adsorption	3.88	3.48	0.22	7.58
	After adsorption	1.37	2.14	0.22	3.73
Organosolv	Before adsorption	2.20	5.73	0.42	8.35
	After adsorption	0.88	2.24	0.16	3.27

Table 4 Elemental analysis and BET measurements of lignins

Elemental analysis

	Nitrogen (%)	Carbon (%)	Hydrogen (%)	Sulphur (%)	Oxygen (%)	O/C
Alkali	0.9	61.5	5.8	2.4	29.4	0.48
Organosolv	0.3	66.2	5.9	–	27.6	0.42

Nirtrogen adsorption-desorption measurements

	BET surface area ($\times 10^{-2}$ m^2/g)	Pore diameter (nm)	Total pore volume ($\times 10^{-4}$ cm^3/g)
Alkali	30.1	10.4	8.1
Organosolv	3.2	3.8	0.7

and 29.4%, respectively. Alkali lignin was also found to contain 2.4% sulfur that was absent in organosolv lignin. Variations in elemental compositions between the two lignins indicate that alkali lignin should have more sites (O- and S-containing functionalities) for H-bonding. On the other hand, the oxygen/carbon mass ratio, O/C, should provide some insight into the polarity of lignin and hence its sorption capacity (Wei and Seo, 2010). However, elemental analysis of studied lignins showed little difference in the O/C ratio i.e., 0.42 for organosolv and 0.48 for alkali lignins (Table 4).

Table 4 also summarizes specific surface areas, pore volumes and pore diameters of the two lignins obtained by the BET method. The average pore diameters as determined by BJH method were 10.4 and 3.8 nm for alkali and organosolv, respectively. The BET surface area and calculated total pore volume of alkali lignin were almost 10 times greater than that of organosolv lignin suggesting that alkali lignin should provide more sites for sorption.

^{31}P NMR data shown in Table 3 also indicated that the total content of –OH groups in both organosolv and alkali lignins was quite similar, i.e., 8.35 and 7.58 mmol/g, respectively, but the type of –OH groups was quite different. For example, organosolv lignin contained more phenolic-OH groups than alkali lignin, i.e. 69% and 46%, respectively. The variations in the type of –OH groups between the two lignins might have affected the strength of H-bonding between DNAN and the type of lignin used. For example, organosolv lignin with more phenolic-OH than the alkali lignin provided stronger sorption sites (H-bonding) which is in line with the observation of high sorption energy ΔH^0 in the case of organosolv lignin (Table 2).

3 Conclusions

In conclusion, organosolv and alkali lignins were successfully used to remove DNAN from water with alkali lignin acting as better sorbent exhibiting faster sorption kinetics. Low cost of lignin and it's rapid and efficient removal of DNAN from water may constitute the bases for the development of a cost-effective technology for the treatment of industrial wastewaters.

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