ADSORPTION OF DYE POLLUTANTS BY GREEK LIGNITE: A PRELIMINARY EXPERIMENTAL STUDY[1]

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ABSTRACT

Adsorption processes are widely used to remove pollutants from wastewaters. The present study presents the preliminary results of an investigation conducted on color removal from an azo dye, Acid Orange 7, by adsorption onto raw lignite, as well as the catalytic effect of lignite in the chemical reduction of azo dyes by sulphides. A lignite sample collected from Amynteo region, northern Greece, was chosen for the experimental work. The lignite shows high ash and TOC contents and is rich in huminite and liptinite macerals, while FTIR spectroscopy reveals a great abundance of C=O and C-O-R functional groups. The decolourisation experiment showed that lignite did not accelerate the chemical reduction of azo dyes by sulphides and only a poor adsorption onto lignite has been addressed. Further investigation is proposed conducting the experiment under different parameters (pH, temperature, particle size etc.). Other adsorbents, such as Greek lignites and peats with different chemical characteristics from Amynteo lignite, demineralised and oxidized lignite and lignite coke are suggested to be used in order to assess the feasibility of the adsorption procedure.

ΛΕΞΕΙΣ-ΚΛΕΙΔΙΑ: περιβαλλοντική μηχανική, λιγνίτης, προσρόφηση, ρυπαντές, συνθετικά χρώματα
KEYWORDS: environmental engineering, lignite, adsorption, pollutants, dyes

ΠΕΡΙΛΗΨΗ

Στην παρούσα εργασία διερευνήθηκε η προσροφητική ικανότητα του Ελληνικού λιγνίτη και η καταλυτική επίδραση που μπορεί να έχει στον αποχρωματισμό πλούσιων σε συνθετικές χρωστικές ουσίες υδάτων. Το λιγνιτικό δείγμα που χρησιμοποιήθηκε, συλλέχθηκε από το λιγνιτικό κοίτασμα Αμυνταίου και έλαβε με κονιοποίηση τη μορφή λεπτομερούς σκόνης. Τα βασικά χαρακτηριστικά του λιγνίτη είναι οι σχετικά υψηλές περιεκτικότητες σε τέφρα (20% επί ξηρού) και Ολικό Οργανικό Άνθρακα (68% επί δείγματος ξηρού, απαλλαγμένου τέφρας), ενώ η ανθρακοπετρογραφική του σύσταση φανερώνει σχετικά υψηλή περιεκτικότητα σε χουμινίτη (83% επί ξηρού, απαλλαγμένου ανόργανων ενώσεων) και λιπτινίτη (12% επί ξηρού, απαλλαγμένου ανόργανων ενώσεων) και μικρή σε ινερτινίτη (4.5% επί ξηρού, απαλλαγμένου ανόργανων ενώσεων). Με τη χρήση της φασματοσκοπίας υπερύθρου (Fourier Transform Infrared Spectroscopy-FTIR) έγινε εμφανής η παρουσία C=O και C-O-R δομικών μονάδων με τη μορφή έντονων κορυφών στην περιοχή 1800-1000 cm^{-1}. Έλαβε χώρα ασυνεχές πείραμα (batch experiment), κατά το οποίο παρασκευάστηκαν εννέα συνολικά φιάλες: τέσσερις που περιείχαν χρωστική ουσία (Acid orange 7), διαφορετικές ποσότητες λιγνίτη και Na_2S σουλφίδιο, δύο φιάλες που περιείχαν χρωστική ουσία και λιγνίτη και τρεις φιάλες που περιείχαν χρωστική ουσία και Na_2S σουλφίδιο. Η διαδικασία αποχρωματισμού στις φιάλες υπολογίστηκε μετά από μία, τέσσερις και οκτώ μέρες, με βάση την απορρόφηση υπεριώδους ακτινοβολίας στα 484 nm. Χρησιμοποιήθηκε φασματοφωτόμετρο Milton Roy Spectronic 601. Τα αποτελέσματα έδειξαν ασήμαντη καταλυτική δράση στην χημική αναγωγή της χρωστικής ουσίας από το Na_2S σουλφίδιο και μικρή προσρόφηση της χρωστικής ουσίας στο λιγνίτη ως έχει. Με βάση τις ενδείξεις της πρόδρομης αυτής μελέτης, κρίθηκε απαραίτητη η περαιτέρω έρευνα σε διαφορετικές πειραματικές συνθήκες (pH, θερμοκρασία, κ.λ.π.) και με χρήση δειγμάτων λιγνίτη ή τύρφης, που αφθονούν στον Ελληνικό χώρο, με διαφορετικά ποιοτικά χαρακτηριστικά, είτε δηλ. δειγμάτων λιγνίτη ελευθέρου ανόργανων ενώσεων είτε λιγνιτικού κωκ που θα παραχθεί από Ελληνικούς λιγνίτες.

1:ΠΡΟΣΡΟΦΗΣΗ ΧΡΩΜΑΤΙΚΩΝ ΡΥΠΑΝΤΙΚΩΝ ΟΥΣΙΩΝ ΑΠΟ ΕΛΛΗΝΙΚΟΥΣ ΛΙΓΝΙΤΕΣ: ΜΙΑ ΠΡΟΔΡΟΜΗ ΠΕΙΡΑΜΑΤΙΚΗ ΜΕΛΕΤΗ

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Ταυτόχρονα, διερευνάται η καταλυτική επίδραση του λιγνίτη στον αποχρωματισμό χρωστικών ουσιών από ενεργοποιημένη ιλύ σε αναερόβιους αντιδραστήρες.

INTRODUCTION

The objective of wastewater treatment has expanded considerably from simple nuisance control to include public health, environmental, aesthetic and ecological considerations (Reible, 1998; Corbitt, 1999). Adsorption processes are widely used to remove pollutants from wastewaters and waste gases (Tschobanoglous and Burton, 1991; Hammer and Hammer, 1996). More recently, awareness and concern has increased as to the long term toxic effects of water containing dissolved metal ions and organic compounds. The problem is more severe for the textile industry because of its dynamic nature. Constantly changing process lines result in diverse and complex wastes that are ever changing in constitution and colour. Dyes are synthetic organic aromatic compounds that are molecularly dispersed and bound to the substrates by intermolecular forces and have high application potential in the industrial sector as colouring material. The textile industry ranks first in the consumption of the dyes and the effluents released from textile dyeing are intensively colored and pose serious problems to various segments of the environment. The persisting color, non-biodegradable, toxic and inhibitory nature of spent dyebaths has considerable deleterious effects on the water and soil environment (Venkata Mohan et al., 1999).

Adsorption and chemical treatment processes have shown promise as practical and economic process for treatment of textile waste; especially for color removal (Hoo et al., 2000). Activated carbon, coke special oxides and macroporous organic polymers are the most common adsorbents in industrial use (Henry and Heinke, 1996; Lekkas, 1996). A prerequisite for technical application of adsorption processes is the availability of suitable and cheap adsorbents (Wiessner et al., 1998). Active carbons are effective adsorbents for the removal of dissolved organic or mineral substances from wastewater (Taylor et al., 1998). The adsorptive capacities of solids are essentially attributed to the internal surface area, porosity and surface reactivity which is linked to the texture of the surface, ashes content and to the surface functional groups involved both in chemisorption and physisorption (van Krevelen, 1993; Finqueneisel et al., 1998).

Even though color removal by adsorption onto activated carbon is highly efficient and reliable, the overlying cost of the activated carbon and associated problems of regeneration and reuse warrants search for alternative low cost adsorbents. In this process, various materials derived from industrial waste materials, agricultural wastes, minerals, coal, soil etc. have been widely investigated for textile dye color removal (Gupta et al., 1988; Namasivayam and Yamuna, 1992). The incorporation of peat and lignite in wastewater treatment has received increasing attention and currently offers a very attractive method of pollution remediation. Besides being plentiful, inexpensive and available in many countries, both of these materials possess several characteristics that make them effective media for adsorption processes. Peat and lignite used in this way could be regenerated and reused, and both have the potential to be used as starting materials for the production of chars and activated carbons (Allen et al., 1997). The vast porosity of lignites facilitates access to the functional groups and increases the total surface area available for adsorption to take place. Gaydardjiev et al. (1996) have reported the feasibility of removal of organic reagents from solvent extraction effluents by adsorption onto lignite.

The aim of the present study was to investigate the adsorption capacity of raw lignite concerning dye removal from wastewaters and its catalytic effect in the chemical reduction of azo dyes by sulphides.

EXPERIMENTAL

Materials

Lignite from Amynteo coal basin, northern Greece, was selected for this experimental work. Lignite sample was finely ground and proximate (moisture, ash, total organic carbon-TOC), ultimate (C, H, N, S, O) and coal petrographical (huminite, liptinite, inertinite) analyses were performed. The organic structure of Amynteo lignite was also determined by Fourier Transform Infrared Spectroscopy (FTIR). Specimen for FTIR was prepared using potassium bromide (KBr) pellet technique. A very small amount of the lignite sample (approx. 0.5 mg) was mixed with 200 mg KBr to produce the pellet. A Nicolet 510P spectrometer was employed, equipped with a DTGS detector, at a resolution of 4 cm^{-1}. Spectra were recorded by co-adding 128 scans. The infrared signal was recorded in the region between 400 and 4800 cm^{-1} wavenumber.

Acid Orange 7 azo dye was employed as the test dye.

Batch Experiments

Batch experiments were performed at room temperature employing different amounts of raw lignite adsorbents. The experiment aimed to determine whether lignite could accelerate the reduction of the azo dye Acid Orange 7 by sulphide. Experiments were done in 50 ml glass bottles, containing 47.4 ml of $NaHCO_3$ bicarbonate buffer (5 g/l), different amounts of lignite (2.7 mg - 34 mg) and 1ml of 100 mM Na_2S sulphide. The concentration of the dye in each bottle was adjusted to 200 mg/l. Demineralized water was added up to 50 ml. Before addition of the sulphide, the headspace in the bottles was changed to N_2/CO_2 (70%/30%). In particular, the following bottles were produced:

a) 4 bottles with 200 mg/l Acid Orange 7 dye (AO7), different amounts of lignite and 100 mM sulphide,
b) 2 bottles with 200 mg/l AO7 dye and lignite, without sulphide, in order to correct for possible adsorption of the dye to the lignite,
c) 3 bottles with 200 mg/l AO7 and 100 mM sulphide, without lignite, in order to assess the rate of non-accelerated Acid Orange 7 dye reduction by sulphide.

All bottles were stored in an incubator and periodical measurements of the residual colour were conducted. Decolourisation was measured using a Milton Roy Spectronic 601 UV spectrophotometer at the wavelength of maximum absorbance (484 nm).

The adsorption experimental work was conducted in the laboratories of the Department of Environmental Technology, Wageningen University of Life Sciences, The Netherlands. The experiment was incorporated into the ongoing research of the Department of Environmental Technology, concerning the investigation of several mediating compounds and adsorbents in wastewater treatment. FTIR spectroscopy, chemical and petrographical analyses, were performed at the Institute of Geology and Geochemistry of Petroleum and Coal, RWTH University of Technology of Aachen, Germany.

RESULTS AND DISCUSSION

The chemical characteristics of the lignite sample are shown in Table 1. The organic functional groups of the lignite sample, as determined by FTIR spectroscopy, are indicated in Figure 1. Amynteo lignite sample shows high ash and Total Organic Carbon (TOC) contents, is rich in huminite macerals and has relatively high liptinite contents. FTIR spectroscopy reveals a great abundance of C=O and C-O-R functional groups (in the 1800-1000 cm^{-1} region).

Table 1. Principal characteristics of the lignite sample.

Sample	Moisture %db	Ash %db	TOC %daf	C %daf	H %daf	N %daf	O %daf	S %daf	Hum %dmmf	Inert %dmmf	Lipt %dmmf
Lignite	11.1	20.0	67.9	63.0	4.6	2.1	27.9	2.4	83.3	4.5	12.2

db=dry basis; daf=dry, ash-free basis; dmmf=dry, mineral matter-free basis; Hum=huminite; Inert= inertinite; Lipt=liptinite

The amount of AO7 dye adsorbed by different quantities of lignite as a function of adsorption time is shown in Figure 2. The comparison of the nine decolourisation curves of the above mentioned figure reveals that lignite did not accelerate the chemical reduction of azo dyes by sulphides. If this was the case, then the decolourisation of AO7 should have proceeded faster in bottles (a) than in bottles (c). The extent of the adsorption of AO7 dye increases with rise of the amount of lignite added. The adsorption capacity of lignite is estimated by looking at the form of the decolourisation curve for bottles (b), as well as at the difference of decolourisation curves between bottles (b) and (c). The rate of removal of colour was rapid initially (after one day). The rate levelled off gradually then attained a more or less constant value beyond which there was no significant increase in colour removal. The instantaneous adsorption is probably attributed to the involvement of surface acidic functional groups leading to chemisorption of dye molecules (Venkata Mohan et al., 1999). The highest concentration of lignite applied was 35 mg lignite in 50 ml liquid (i.e. 700 mg lignite per litter). We can roughly estimate that lignite adsorbed only 5% of the originally added AO7 dye. A similar concentration of activated carbon would have adsorbed 10-15% of AO7 dye (Zee et al., 2000a). The overall adsorption is a combination of primary and secondary adsorption, where smaller organic compounds were adsorbed to an already adsorbed layer of bigger organics (Wiessner et al., 1998).

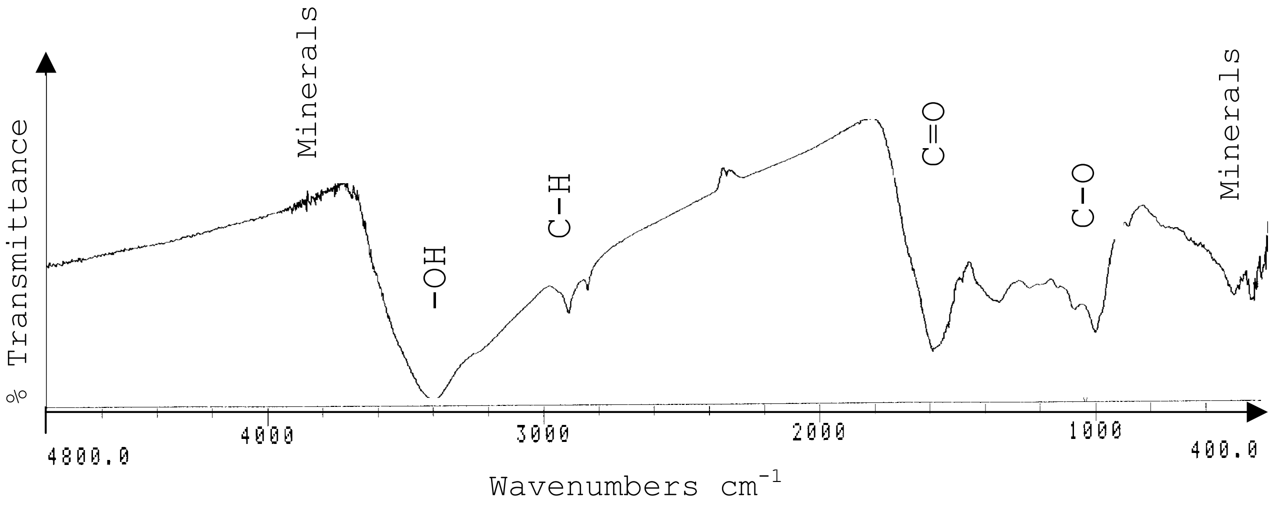

Figure 1. FTIR spectra of the lignite sample. Different functional groups and minerals are indicated upon the spectra.

There is a great number of parameters that may affect an adsorption experiments. These parameters, such as pH, mass of the adsorbent, temperature, ash content etc., should be taken into consideration and are discussed below.

According to Venkata Mohan et al. (1999), the sorptive removal of dye from aqueous solution is rather complex, involving both boundary layer diffusion and intraparticle diffusion. Adsorption process is dependent upon mass of the adsorbent, the pH conditions of the system and requires optimum pH for maximum colour removal. The same authors stated that there is an influence of pH of the dye solution on sorptive uptake by a sorbent. The dye uptake is less at lower pH. As the pH of the dye solution increases, dye uptake also increases considerably. The influence of the pH of the solution on the adsorption capacities has also been reported by Finqueneisel et al. (1998). Gaydardjiev et al. (1996) stated that there is an optimal concentration of lignite and further increase does not lead to enhanced removal. This is also clearly shown in our experiment.

The adsorptive properties are strongly dependent on the initial lignite precursors and ashes content and composition are of great importance (Finqueneisel et al., 1998). The increasing sorption capacity corroborates well with decreasing carbon content and increasing ash content of the coal adsorbents (Venkata Mohan et al., 1999). According to Gaydardjiev et al. (1996), adsorption experiments using different maceral groups of the lignite showed no significant difference in their performance compared to that of raw lignite.

Gürses et al. (1995) noticed that there is an evident effect of temperature on the adsorption process. Higher temperatures may cause higher adsorption, due to the increase at the rate of diffusion through the pores at higher temperature. According to Allen et al. (1997), larger particle size ranges cause a decrease in the surface area available for adsorption. This decrease in surface area results in a reduced number of available sites for sorption, the dye molecules tend to adsorb onto the surface and then diffuse into the particle more readily.

The vast porosity of low rank coals facilitates access to the functional groups and increases the total surface area available for adsorption to take place (Gaydardjiev et al., 1996). Oxygenated surface groups improve sensibly the adsorption of the organic compounds (Finqueneisel et al., 1998). Such functional groups are clearly indicated in the FTIR spectra of Amynteo lignite.

Allen at al. (1997) have investigated the adsorptive capacities of peat and lignites. They concluded that the adsorption of dyes onto lignite was smaller than those obtained for the dye/peat adsorption systems and is attributed (i) to the topography of the sorbent particle surface, suggesting that the surface of the lignite particle is more heterogeneous than that of peat, thus causing an increase in the film boundary layer or (ii) the surface chemistry of the adsorbents, such that the force of attraction of peat particles for the dye molecules in solution is greater than that of lignite.

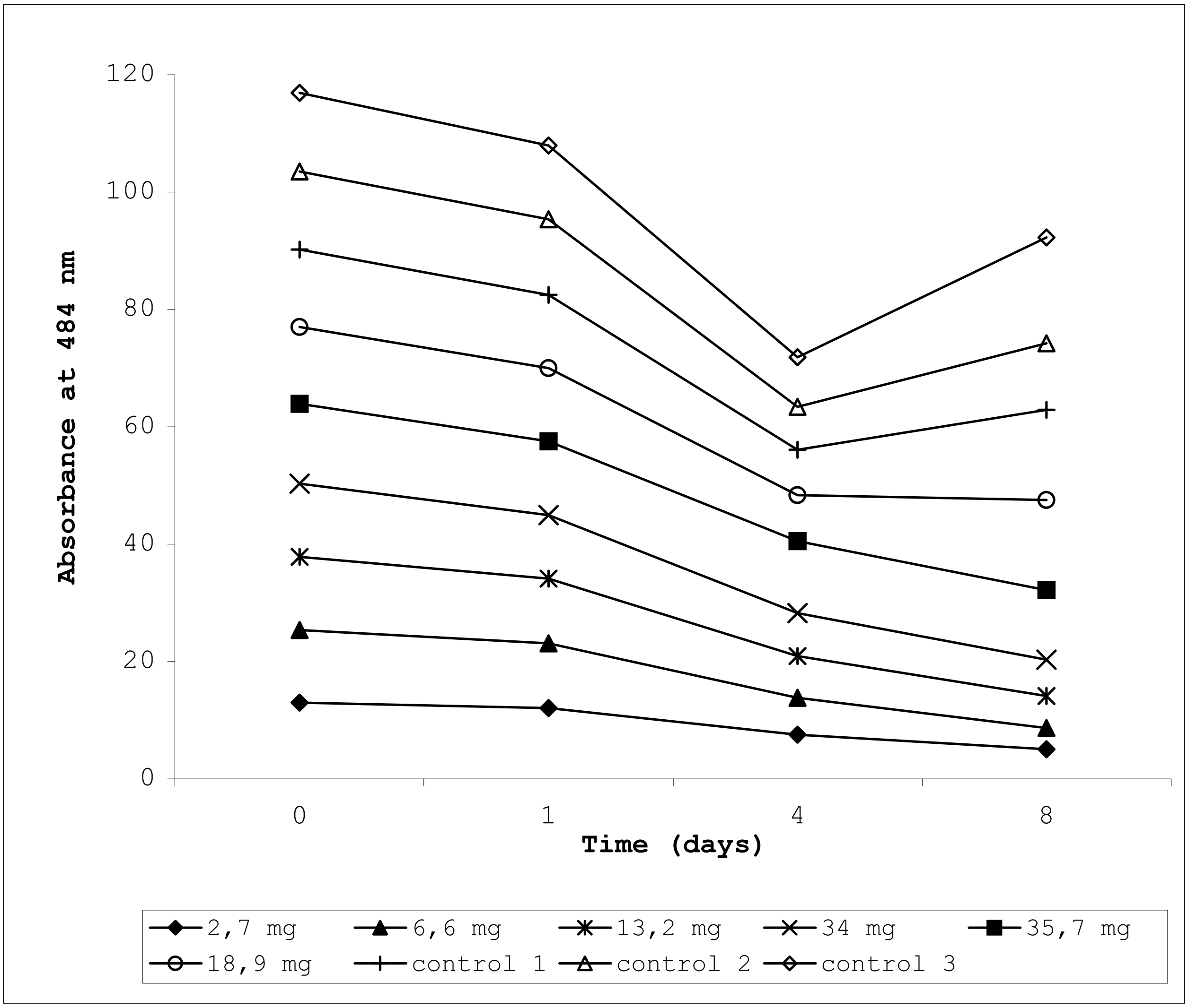

Figure 2. Decolourisation of Acid Orange 7 azo dye using different amounts of lignite.

Except raw lignites, different kinds of adsorbents, produced by lignites should also be considered. Adsorbents are generally seen as materials with a high surface area and with a highly porous structure. A charring and activation process should therefore maximise the surface area and pore volume of the adsorbent in order to encourage the development of micro- and meso-pore structures (Allen et al., 1997). Demineralized and oxidized lignite samples may have decreased adsorptive capacities. In the case of oxidized samples, the adsorbed oxygen may block the micropores, while in demineralised samples, there is a removal of the hydrophilic mineral matter, which may promote the adsorption (Gürses et al., 1995). The strong increase due to oxidation may be attributed to carboxylic surface groups (Finqueneisel et al., 1998). According to Wiessner et al. (1998), the adsorption affinity of activated carbon for dissolved organic materials correlates directly with the number of acidic functions normalized by molecule size, up to a limit beyond which further increases in acidity enhance the solubility of the organic macromolecules too much to allow additional adsorption to occur. The application of activated coke in conjunction with further treatment steps to purify contaminated wastewater seems to be economically feasible.

It is generally suggested to investigate the adsorption capacities of Greek lignites and peats with different chemical characteristics, demineralized and oxidized lignite and lignite coke. The effect of lignite in the anaerobic reduction of dyes using bioreactors with activated sludge is also being investigated. A similar experimental work has been previously described by Zee et al. (2000b).

CONCLUSIONS

Adsorption processes are widely used to remove pollutants from wastewaters. In the present study a lignite sample collected from Amynteo region, Northern Greece, was chosen to investigate the possibility of color removal from an azo dye, Acid Orange 7, by adsorption onto this raw lignite, as well as the catalytic effect of lignite in the chemical reduction of azo dyes by sulphides. The lignite sample shows high ash and TOC contents and is rich in huminite and liptinite macerals, while FTIR spectroscopy reveals a great abundance of C=O and C-O-R functional groups. The decolorisation experiment showed that lignite did not accelerate the chemical reduction of azo dyes by sulphides. Only a poor adsorption onto lignite has been addressed. Further investigation is proposed conducting the experiment under different parameters (pH, temperature, particle size etc.). Other adsorbents, such as Greek lignites and peats with different chemical characteristics from Amynteo lignite, demineralised and oxidized lignite and lignite coke are suggested to be used in order to assess the feasibility of the adsorption procedure.

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