The Interest of multidimensional analysis to evaluate the physicochemical characterization of raw margines in oil mills in Ouezzane Region (North of Morocco)

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ABSTRACT*:* The olive oil industry In addition to oil as a main product generates large quantities of waste (oils, margins) that are harmful to the environment due to their chemical composition and very high polluting power. The aim of this work is to study the physico-chemical characterization of margines generated by the production of virgin olive oil in the region of Ouezzane (Morocco). A physico-chemical study was carried out to do it. This is based on the determination of the physicochemical parameters of the raw margins of two systems: continuous and discontinuous.

The obtained results showed that the margins present a worrying degree of organic pollution and an important mineralization. The Analysis by Principal Component Analysis (PCA) of the physico-chemical data allowed us to detect correlations between the different parameters and to differentiate a typology of the quality of the margins in the study region. The system of discontinuous extraction is more polluting than the one of continuous modern extraction which is explained by the different in remarkable concentration of COD, BOD5.

Indeed, the discharge of margins to the receiving environment creates a real environmental problem. In order to solve this problem, we recommend the proper management of the oil mill discharge by installing a local sewage treatment plant.

Key Words: Margins, Extraction System, ACP, CAH, Ouezzane, Morocco.

1 Introduction

In parallel with the production of olive oil, the producing countries reject two by-product wastes in the nature, one of which is solids called pomace and the other is a black liquid effluent called margins or Sewage from olive oil factory [1-5]. The latter is a real environmental problem, especially in the Mediterranean basin (Spain, Italy, Greece, Turkey, Syria, Tunisia and Morocco).

About 6 * 10^3 m^3 of these effluents are produced annually worldwide, of which 98% is produced in the Mediterranean basin [6]. In Morocco, it was estimated that olive oil and margines are respectively 1 000 000 tonnes, 100 000 tonnes and 580 000 m^3 for an area of 580 000 ha for 2003-2004 of olives, [7]. This is accompanied by the production of a large amount of solid and liquid waste for a short period (November to March) [8, 9]. The production of olives is very important in all regions of Ouezzane, which is due to large areas of olive tree which reflects the great efforts of the State in terms of Green Morocco Plan. Extraction of olive oil is mainly carried out by two processes: discontinuous (pressing) or continuous (centrifuging) [10]. Generally, estimations show that a kilogram of olive provides 1 to 1.5 liters of liquid effluent [1, 2]. The

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quality and quantity of margines depend on the extraction of olive oil because they are also influenced by olive variety, harvest season, fruit ripening rate and climatic conditions [3, 4]. They are characterized by an acidic pH (3-5) and a very rumbling electrical conductivity [5]. Because of their composition of water (83-96%), organic matter (3.5-15%), and mineral salts (0.5-2%) [11, 12], of which 80% are soluble (phosphates and chlorides) and 20% insoluble (carbonates and silicates). The most abundant elements are potassium (47%), phosphates (14%), and sodium (7%). [13]

Although these methods are prohibited in Many Mediterranean countries [14-18], these effluents or vegetation waters are discharged directly into uncontrolled sewers, valleys and ponds due to the current lack of adequate treatment technologies for olive oil effluents. The inadequate and uncontrolled disposal methods for these effluents in water bodies are of environmental concern as these effluents contain a significant amount of COD (20-80 g / l) and BOD concentrations, which range from 200 to 400 times than that of municipal waters [19] with a high amount of growth inhibiting microbial compounds such as phenolic compounds and tannins [18, 20, 21]. In this study, we tried to evaluate the quality of the effluents of the olive crushing units in order to determine their degree of pollution, starting from the Ouazzane region.

2 Materials and methods

2.1 Sampling

The marginal samples were ceased from an industrial unit (three- and two-phase system), which is located in the Ouezzane region, in the open olive growing season 2016-2017, from the marginal storage basin transported in 5 liter drums and stored at 4 °C. The analysis was carried out on receipt at the laboratory. The analytical methods and [22] standards are those recommended by the AFNOR (1996-2007). The physico-chemical parameters: pH, EC, Salinity, O2, % O2 were measured *in situ* during the study period by using a HANNA Instruments type pH meter, HI 9622, WTW conductivity meter LF 330 and WTW Oxi 315i / SET Oximeter. The other parameters studied within the Laboratory and the analysis center are the following: MES, MS, DBO5 was measured by Oxytop at 20 °C, COD by a COD spectrophotometer model 45600, Chlorides (Cl^-) are measured by Mohr volumetric method in the presence of silver nitrate, sulfates (SO_4^{2-}), fluorides (F^-) and nitrates (NO_3^-) are determined by the colorimetric method in the presence of sodium salicylate. The Na^+, K^+, Ca^{2+}, Mg^{2+} were measured by flame photometry and trace elements (Fe^{2+}, Mn^{2+}, Cu^{2+}, Zn^{2+}, Co, Cd^{2+}) by ICP-MS.

2.2 Statistical analysis

All the collected data from the margins of the two systems (continuous and discontinuous) in the Ouezzane region were analyzed statistically. The multivariate statistical approach was based on the Principal Component Analysis (PCA) and an Ascending Hierarchical Classification (CHA). The statistical analysis was carried out on 4 samples and 24 variables as mentioned above by using the XLSTAT 2015 software. This analysis makes it possible to synthesize and classify a large number of data in order to extract the main factors which are at the origin of the simultaneous evolution of the variables and their reciprocal relationship [23]. It makes it possible to highlight the similarities between two or more chemical variables during their evolution.

3. Results and Discussions

3.1 Correlations between variables

The study of the bivariate linear correlations between the studied parameters gives information on the strength of the associations between them. The matrix of the correlations of the 24 parameters measured during our study is presented in Table 1.

The correlation coefficients must be interpreted with caution since the sampling stations have been combined to calculate this matrix.

However, in this table, the significant Pearson correlation coefficients ($p < 0.01$) are greater than 0.5 and they are shown in bold, with interesting correlations are observed.

Table 1: Matrix of correlation between the variables on all studied stations

Variables	pH	Tur	CE	Sal	O2	% en O2	K+	Na+	Mg2+	Ca2+	Fe2+	Zn2+	Mn2+	Cu2+	Cl-	SO4-	NO3-	F-	DCOg/l	I
pH	1																			
Tur	0,5774	1																		
CE	-0,3556	**-0,9669**	1																	
Sal	-0,3334	-0,9391	**0,9851**	1																
O2	-0,3632	**-0,9512**	**0,9886**	**0,9993**	1															
% en O2	-0,3566	**-0,9581**	**0,9953**	**0,9969**	**0,9985**	1														
K+	-0,6604	-0,9200	0,8715	0,9058	0,9137	0,8989	1													
Na+	-0,5699	**-0,9993**	**0,9663**	0,9326	0,9452	**0,9541**	0,9054	1												
Mg2+	**-0,9877**	-0,6980	0,4972	0,4725	0,5009	0,4965	0,7558	0,6913	1											
Ca2+	-0,4466	-0,9472	**0,9639**	**0,9889**	**0,9906**	**0,9830**	**0,9582**	0,9372	0,5734	1										
Fe2+	-0,4892	**-0,9537**	**0,9580**	**0,9817**	**0,9849**	**0,9770**	**0,9699**	0,9434	0,6121	**0,9988**	1									
Zn2+	**-0,9801**	-0,6849	0,4765	0,4291	0,4603	0,4629	0,6952	0,6830	**0,9908**	0,5209	0,5601	1								
Mn2+	**-0,9864**	-0,6934	0,4886	0,4532	0,4830	0,4819	0,7291	0,6890	**0,9980**	0,5501	0,5891	**0,9974**	1							
Cu2+	**0,9849**	0,6910	-0,4848	-0,4454	-0,4757	-0,4758	-0,7181	-0,6874	**-0,9961**	-0,5406	-0,5797	**-0,9988**	**-0,9997**	1						
Cl-	-0,5898	**-0,9923**	**0,9615**	**0,9546**	**0,9646**	**0,9647**	**0,9600**	**0,9871**	0,7075	**0,9736**	**0,9804**	0,6780	0,6953	-0,6899	1					
SO4-	-0,2929	-0,9400	**0,9937**	**0,9957**	**0,9953**	**0,9977**	0,8706	0,9366	0,4371	**0,9727**	**0,9635**	0,4043	0,4227	-0,4167	0,9449	1				
NO3-	-0,2301	-0,8958	**0,9695**	**0,9936**	**0,9888**	**0,9851**	0,8660	0,8886	0,3737	**0,9722**	**0,9599**	0,3251	0,3518	-0,3430	0,9148	**0,9907**	1			
F-	-0,2447	-0,7996	0,8709	0,9425	0,9332	0,9135	0,8867	0,7824	0,3683	0,9495	0,9394	0,2849	0,3300	-0,3150	0,8538	0,9143	**0,9561**	1		
DCOg/l	-0,5429	**-0,9796**	**0,9659**	**0,9727**	**0,9796**	**0,9761**	**0,9682**	**0,9722**	0,6640	**0,9902**	**0,9943**	0,6242	0,6468	-0,6396	**0,9958**	**0,9594**	0,9414	0,8979	1	
DBO5g/l	-0,4667	-0,9474	**0,9584**	**0,9847**	**0,9869**	**0,9786**	**0,9653**	0,9368	0,5911	**0,9997**	**0,9996**	0,5375	0,5673	-0,5576	**0,9753**	**0,9666**	**0,9660**	0,9477	**0,9914**	
MESg/l	0,5530	**0,9652**	-0,9500	**-0,9678**	**-0,9737**	**-0,9666**	**-0,9809**	**-0,9554**	-0,6701	**-0,9923**	**-0,9970**	-0,6221	-0,6491	0,6404	**-0,9896**	-0,9484	-0,9376	-0,9140	**-0,9977**	
MSg/l	-0,4459	-0,9359	**0,9533**	**0,9848**	**0,9858**	**0,9761**	**0,9621**	0,9245	0,5707	**0,9992**	**0,9982**	0,5134	0,5451	-0,5348	**0,9669**	**0,9654**	**0,9695**	**0,9583**	**0,9862**	
Co mg/l	-0,4380	-0,6536	0,6580	0,7676	0,7614	0,7250	0,8831	0,6259	0,5101	0,8330	0,8371	0,3996	0,4594	-0,4395	0,7422	0,7055	0,7641	0,9085	0,7880	
Cd mg/l	-0,1027	-0,7699	0,8768	0,9406	0,9279	0,9131	0,8148	0,7560	0,2380	0,9233	0,9060	0,1627	0,2032	-0,1897	0,8142	0,9246	**0,9678**	**0,9863**	0,8617	

The values in bold are different from 0 to a significance level

alpha = 0.05

A strongly negative correlation between the pH and the parameters of Mg2 +, Zn2 + and Mn2 + (r = -0.98) and strongly positive with Cu^{2+} (r = 0.98) was noticed. Strong and positive correlations are observed between the electrical conductivity and the major elements Na^{+}, K^{+}, Ca^{2+}, Cl^{-}, SO_4^{2-}, NO_3^{-} (r between 0.87 and 0.99) as well as with salinity, O_2, COD, BOD_5, MS and Fe (r between 0.95 and 0.98). Other strong and positive correlations between the COD and the parameters CE, Salinity, O_2, Na^{+}, K^{+}, Ca^{2+}, Fe^{2+}, Cl^{-}, SO_4^{2-}, NO_3^{-} r ranging from 0.96 to 0.99) and strongly negative with Turbidity (r = -0.97).

Table 2: Results of the physicochemical analyzes of the margins of the continuous and discontinuous system

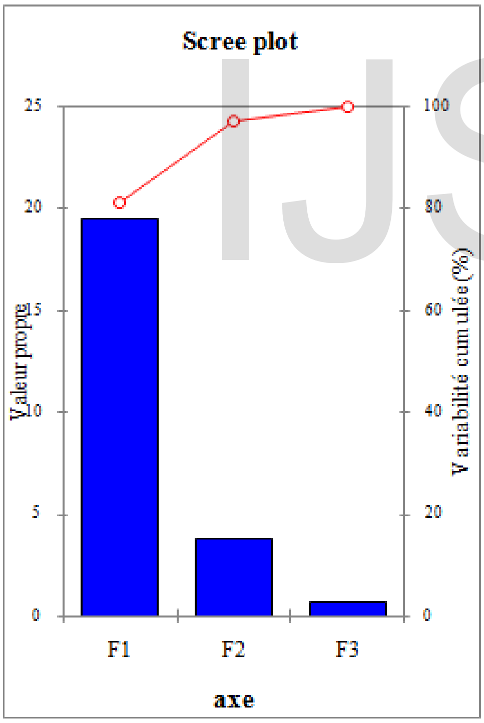
Variable	Observations	Minimum	Maximum	Moyenne	Mean SD
pH	4	4,3300	4,6700	4,5600	0,1571
Tur	4	17,5000	21,5000	19,4250	1,8857
CE	4	10,3300	17,2200	14,0875	3,2724
Sal	4	7,1000	12,7000	9,7750	2,7439
O2	4	1,2000	2,6400	1,9075	0,7136
K+	4	7,8000	17,1000	12,5500	4,4546
Na+	4	1,6200	1,9000	1,7675	0,1300
Mg2+	4	1,4500	2,7200	1,8675	0,5761
Ca2+	4	1,3400	2,3500	1,8200	0,5503
Fe2+	4	0,0300	0,1340	0,0815	0,0578
Zn2+	4	0,0290	0,0630	0,0380	0,0167
Mn2+	4	0,0090	0,0140	0,0105	0,0023
Cu2+	4	0,0086	0,0099	0,0095	0,0006
Cl-	4	1,3000	1,6300	1,4625	0,1666
SO4-	4	0,4200	0,6000	0,5100	0,0841
NO3-	4	0,0110	0,0290	0,0190	0,0085
F-	4	0,5000	0,6400	0,5650	0,0624
DCO g/l	4	45,0000	125,0000	85,0000	43,3974
DBO5 g/l	4	40,0000	100,0000	69,2500	32,6943
MES g/l	4	1,1000	8,2000	4,7000	3,9302
MS g/l	4	55,0000	140,0000	96,2500	44,9768
Co mg/l	4	1,2200	1,6000	1,4550	0,1686

3.2 Principal Component Analysis

Table 3: Eigenvalues and percentages expressed by the main axes.

	F1	F2	F3
Earnings	19,5042	3,7784	0,7174
Variability (%)	81,2674	15,7433	2,9893
Variability %	81,2674	97,0107	100,0000

The analysis of the CPA results also made it possible to calculate the eigenvalues and the variances expressed for each factor and their cumulation (Table 3) (Figure 1). The analysis on the F1-F2 factorial plane showed the general trends. Indeed, the factor F1 has an expressed variance of 81.27%, which is the most important. Then comes the factor F2: with 15.74% of the expressed variance. The cumulative variance expressed is 97.01% for both factors.



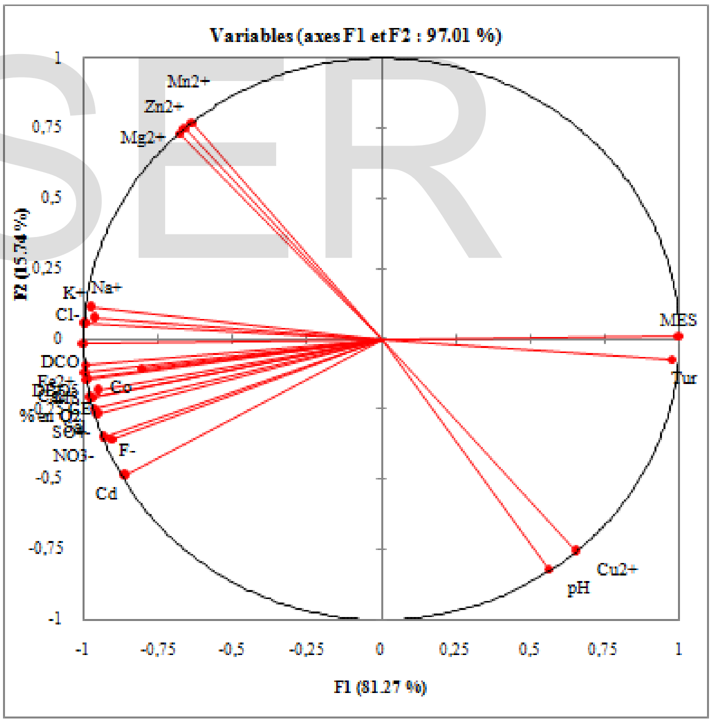


Fig 1: Eigenvalues and percentages expressed for the main axes Fig 2: Analysis in space of variables (factor plane F1-F2)

The component (F1) accounting for 81.27% of the variances consists mainly of MES and Tur in the positive part, mineral variables (CE, Na^+, K^+, Cl^-, NO_3^-, SO_4^{2-}, F^-) organic compounds (BOD_5, COD); the O_2 and the trace elements (Cd, Co, Fe) are located in the negative part of the component. This component shows 18 variables whose coefficients are greater than 0.97 for the MES and the Tur, and less than -0.86 for the other parameters.

Component 2 (15.74% of the variance) is constituted in its positive part by certain metals (Mn^{2+}, Mg^{2+}, Zn^{2+}). Its negative part is composed of the variables pH and Cu^{2+}. In light of these results, many significant correlations have been identified between all the variables measured and have more or less solid correlations between them.

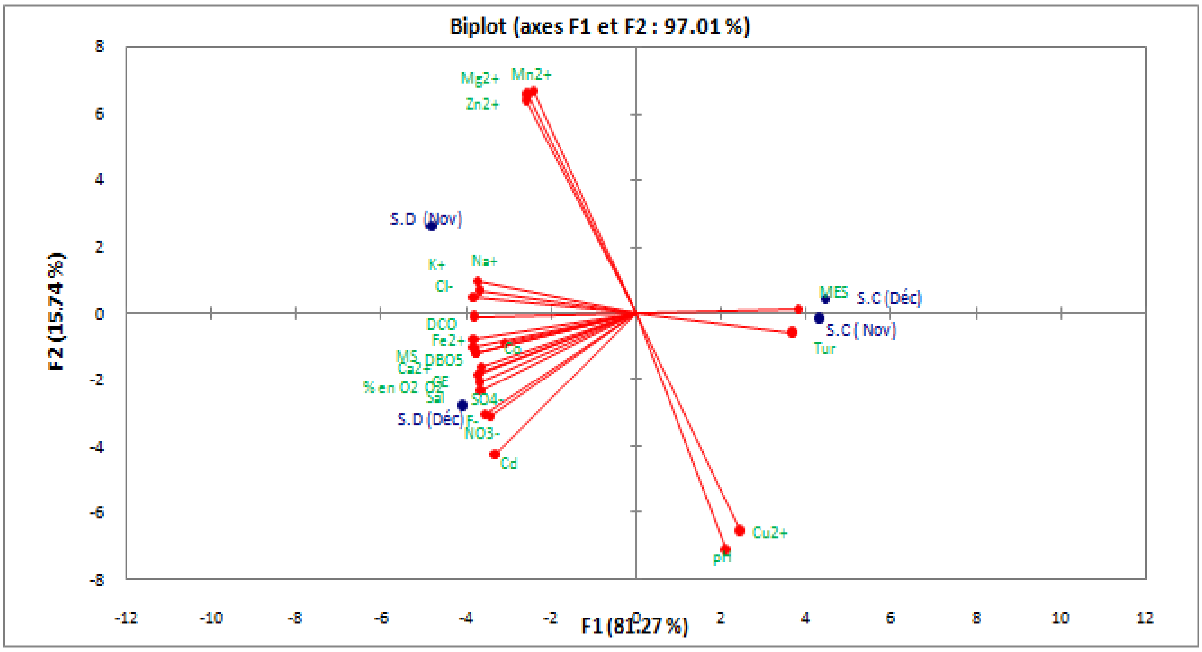


Fig 3: Representations of individuals and variables on the factorial plane F1-F2 (97.01%)

We have a right-to-left distribution of pollution, in this projection, from the continuous system SC to a discontinuous system SD which has a very high pollution load such as BOD_5, DCO, CE, NO_3^- and mineral salts that decrease towards the line presented by the continuous system SC.

3.3 Ascending Hierarchical Classification (CHA)

This classification which is considered as complementary to the ACP and the AFC starts from *n* points considered in isolation and proceeds by producing partitions less and less fine. That is to say, it constructs a sequence of partitions into *n* classes, n-1 classes, n-2 classes, nested in one another, in the following way: by grouping two classes of a partition into *k* classes, we will obtain a partition in k-1 classes and so on.

We speak of hierarchical classification (or hierarchy) because each class of a partition is included in a class of the next partition. The sequence of the obtained partitions is usually represented in the form of a classification tree, referred to as a "hierarchical tree" or "dendrogram".

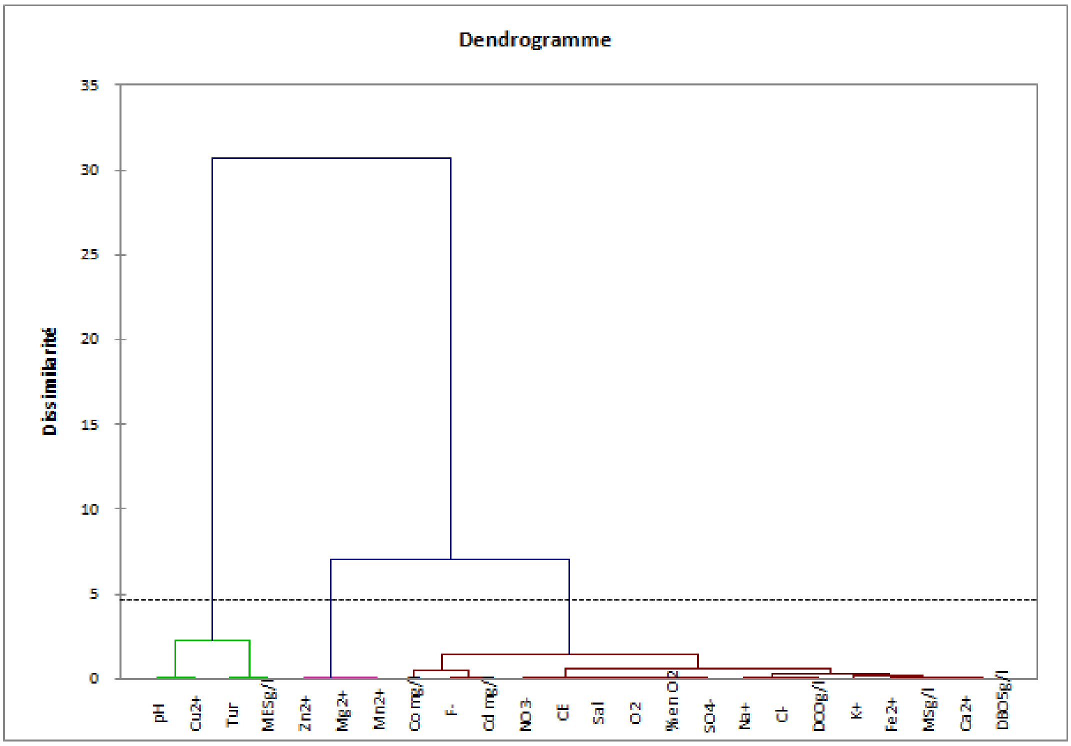


Fig. 4. Dendrogram of the liquid effluents (margines) of the two continuous and discontinuous systems of the Ouezzane Region (Morocco).

To confirm the correlations between the parameters, a HAC was performed from the initial dataset. The cluster search among the variables is indeed a complementary way of studying the latent structure of the data matrix and makes it possible to compare the obtained results with those provided by the PCA. The application of CAH led to a dendrogram shown in Figure 4. Three clusters were identified. The first cluster corresponds to the first principal component F2 of the ACP. The level of dissimilarity between the other two clusters justifies that they appear according to two different principal components in ACP. The results obtained by ACP and CAH are therefore in agreement.

4. Conclusion

Margins with their physicochemical properties represent one of the most important problems faced by Mediterranean countries because of their harmful effects on ecosystems and because they reject them without any treatment. The diversity of the results obtained from the physico-chemical properties of the margine samples is due to a difference in the quality of the method used in the olive oil extraction process, thus, the practice of salting for preservation Olives, the type of olives and the degree of their maturation. The analysis of the margins studied shows that this is a very acidic effluent (pH_{moy}= 4.56), strongly charged with COD (85 g/l) and BOD_5 (69 g/l).

These contents greatly exceed the contents of the chemical elements of domestic or urban wastewater discharge and the analysis of the mineral fraction of the margins showed a dominance of sodium chlorides due to the excessive use of the commercial salt rich in sodium chloride for preserving the olives before being crushed.

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