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Characterization and Bioavailability of Metallic Trace Elements in Different Organic Waste

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ABSTRACT

It is important to address metabolic and heavy metal issues in organic waste through sustainable development, circular economy principles and effective solid waste management, particularly focusing on composting as a crucial approach recognized in Morocco's Green Generation Plan to reduce waste sent to landfills and mitigate greenhouse effects and gas emissions to fight against environmental pollution. This study aims to elevate the significance of organic waste in agriculture by employing composting technics, thereby mitigating its heavy metal content and safeguarding soil and farmland against various forms of contamination. This approach aligns seamlessly with the principles of sustainable development and the circular economy, advocating for responsible waste management and the augmentation of natural resource value. The findings of the study indicated a decrease in heavy metal levels across all composts, with a minimum values at the end of the composting in Gr compost recorded in all heavy metals analyzed (Pb – 0.1125 mg·kg^{-1}, Cd – 0.08 mg·kg^{-1}, Cr – 2.22 mg·kg^{-1}, Zn – 10.88 mg·kg^{-1}, Mn – 28.85 mg·kg^{-1}, Cu –8.30 mg·kg^{-1}, Fe – 545.18 mg·kg^{-1} and Ni – 1 mg·kg^{-1}). The findings from the assessment of heavy metal levels in the examined compost samples demonstrate their adherence to regulatory standards. Consequently, these composts can be confidently employed as organic soil enhancers, contributing to the enrichment of agricultural soils and fostering plant growth, all while avoiding the potential hazard of undue metal contamination. This study comes to confirm and consolidate previous works findings regarding the valorization of organic solid waste through composting and to minimize their major environmental risks by reducing trace metal elements through this biological process.

Keywords: composting, organic waste, metallic trace elements, heavy metals, biofertilizers.

INTRODUCTION

Composting, acknowledged as a natural process for decomposing organic matter, is considered a sustainable method for managing organic waste and generating beneficial soil amendments [Houot et al., 2009]. However, concerns emerge as trace metals (TMEs) and heavy metals accumulate in organic waste, presenting potential hazards to both the environment and human health. Hence, it is essential to enhance our comprehension of how composting contributes to reducing these contaminants, ensuring the safe and sustainable application of compost [Singh & Kalamdhad, 2012]. Singh & Kalamdhad (2012) highlight the need for a more thorough comprehension of the mechanisms implicated in reducing trace metals (TMEs) and heavy metals throughout the composting process. Consequently, it becomes crucial to investigate the origins of these contaminants, their distinct behaviors throughout composting, and the factors influencing their reduction and removal.

Research shows that TMEs and heavy metals originate from a variety of sources, including industry, intensive agriculture, urban waste and mining activities. These contaminants have the capacity to accumulate in soils, with adverse consequences for ecosystems and potential risks to human health [Wong & Selvam, 2006]. Composting is emerging as a promising solution for reducing these risks. The key mechanisms involved include active microbial degradation, which promotes the transformation of complex organic compounds containing TMEs and heavy metals into less toxic, less mobile forms [Cai et al., 2007]. In addition, the rise in temperature during the composting process facilitates the volatilization of certain volatile heavy metals [He et al., 2009]. Adsorption onto organic matter and minerals present in compost also plays a significant role in reducing the availability of TMEs and heavy metals [Singh & Kalamdhad, 2012].

Nevertheless, for the secure and sustainable utilization of compost, it is essential to conduct precise evaluations of the occurrence and levels of trace metals (TMEs) and heavy metals in composts [Houot et al., 2009]. These assessments contribute to an enhanced comprehension of the factors impacting the reduction of contaminants, guiding composting practices towards optimizing these reductions [Singh & Kalamdhad, 2012].

This study seeks to elucidate the contribution of composting to the elimination and mitigation of trace metals (TMEs) and heavy metals in organic waste. The focus will be on examining the origins of these contaminants, their dynamics throughout the composting process, and the factors that impact their reduction and removal. Additionally, the analytical approach employed to evaluate the presence of these contaminants involved Heavy Metals Analysis by ICP-AES, enabling the determination of levels for Pb, Cd, Cr, Zn, Mn, Cu, Fe and Ni.

Based on these various analyses, the results obtained will enable us to gain a better understanding of the fundamental role of composting in the reduction of TMEs and heavy metals, thus promoting more sustainable management of organic waste and preserving soil and environmental quality. The results of this study will help guide composting practices by providing recommendations for minimizing the environmental impact of these contaminants. By integrating current knowledge and recent discoveries, more effective approaches for the reduction and elimination of TMEs and heavy metals in composts can be developed, thus contributing to a healthier and more sustainable environment for present and future generations.

MATERIALS AND METHODS

Raw materials sampling

Olive pomace (Gr)

Morocco stands as the fifth-largest global producer of olive oil, contributing 140,000 tonnes, equivalent to 5% of the world's total production. Nevertheless, the olive industry gives rise to both liquid waste, in the form of oil mill wastewater, and solid waste, represented by olive pomace [El Kafz et al., 2023]. The study utilized pomace residues sourced from a crushing unit employing a three-phase extraction system, situated in Tiflet, Morocco. Tiflet is a city located in the Khemisset province within the Rabat Salé Kénitra region, characterized by geographical coordinates of 33°53'40″ N latitude, 6°18′23″ W longitude. The town's altitude is approximately 340 meters above sea level [Doughmi et al., 2022].

Poultry manure (F)

Poultry droppings encompass all substances expelled through the digestive and urinary tracts via the poultry cloaca. The collection of this waste was carried out on a poultry farm located in Tiflet [Ameziane et al., 2020].

Organic household waste (D)

Organic household waste originated from the wholesale market situated in the city of Salé, Morocco, with specific geographical coordinates of 34°1'54.476" North latitude and 6°46'17.494" West longitude. The altitude above sea level at this location is recorded at 34 meters [Doughmi et al., 2022].

Green waste (V)

The green waste employed in this investigation originated from gardening activities conducted at the Salé Higher School of Technology in Salé, Morocco. The specific geographic coordinates for this location are 34°03'11" North latitude and 6°47'54" West longitude, with an altitude above sea level recorded at 34 meters.

Chemical analysis

The analyses were conducted at the National Center for Scientific and Technical Research (CNRST) in Rabat. Metal concentrations (Fe, Zn, Cu, Mn, Ni, Cr, Cd, Pb) were assessed using inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Solid samples preparation

This pre-treatment involves two sequential steps before analysis: preparation and mineralization. The sample undergoes drying in an oven at 40°C for a minimum of 16 hours. Subsequently, it is emulsified and passed through a 2 mm sieve. The portion smaller than 2 mm is further ground to achieve a powder with a particle size less than 250 µm [Alsac, 2007]. The acid employed for solid mineralization is a regal water solution, consisting of three parts hydrochloric acid (37% concentration) and one part nitric acid (65% concentration) in a 3:1 ratio. Regal water is capable of dissolving all metals [ISO 15587-1: 2002]. A precisely weighed 0.5 g of dry solid sample is placed into a Digitube digestion tube. Subsequently, 6 ml of hydrochloric acid solution and 2 ml of nitric acid are added to the tube. The sample is then heated to 95°C for 75 minutes using the heating block mineralizer. After cooling to room temperature, the resulting mineralizate is adjusted to a volume of 50 ml with demineralized water.

Expressing results

Results for solid samples are defined as follows:

$$C\ (\mathrm{mg\cdot kg^{-1}}) = [C\ (\mathrm{mg\cdot L^{-1}}) \times V\ (mineralization)\ (\mathrm{L})]\ /mass\ (\mathrm{kg}) \qquad (1)$$

Two comparisons were conducted on distinct levels: firstly, the comparison of ETM contents among various compost types, and secondly, the comparison of ETM contents for different compost types against the threshold concentrations specified in the NF U 44-051 standards [AFNOR, 2006].

Statistical data processing

All parameters examined in this study underwent processing through SPSS software (Statistical Package for the Social Sciences, version 20). The results are expressed as mean ± standard deviation and were subjected to analysis using ANOVA (analysis of variance).

RESULTS AND DISCUSSION

In this study, the results show that the levels of trace metals in the compost samples remain below the recommended limits for safe use in agriculture. The highest concentrations of heavy metals were recorded in the poultry manure compost, with maximum levels after composting of Iron (652.62 mg·kg^{-1}), Copper (45.34 mg·kg^{-1}), Manganese (509.73 mg·kg^{-1}), Zinc (364.46 mg·kg^{-1}) and Nickel (3.33 mg·kg^{-1}) (Figure 1).

On the other hand, as regards heavy metals, the maximum value after composting was recorded in green waste compost for Chromium (10.40 mg·kg^{-1}) and Lead (2.36 mg·kg^{-1}), and in poultry droppings compost for Cadmium (0.27 mg·kg^{-1} (Figure 2). These concentrations all comply with current environmental standards. It should be noted that heavy metal levels vary slightly between some samples, which can be attributed to the diversity of organic matter sources used in their production (Table 1). It's important to note that the effectiveness of composting in reducing metallic trace elements depends on various factors such as the initial composition of the organic waste, the composting method, and the specific characteristics of the metals involved. Regular monitoring and testing of the compost are essential to ensure that it meets quality standards and poses no environmental or health risks. Additionally, not all metallic trace elements may be equally affected by composting, and the success of this process can vary depending on the specific conditions and elements involved (Table 1).

During the composting process, composting can contribute to the reduction of metallic trace elements content in organic waste through several mechanisms, we note that microorganisms play a crucial role in breaking down organic matter. These microorganisms can also interact with metallic trace elements, leading to processes such as immobilization and transformation. Immobilization involves microorganisms incorporating metals into their biomass, reducing the bioavailability of metals in the compost. Transformation processes can convert certain metal forms into less mobile or less toxic forms [Wang et al., 2022]. Composting can alter the pH of the material being composted. The pH of the composting environment can influence the solubility and mobility of metallic trace elements. In many cases, composting tends to create conditions that decrease the leachability and mobility of metals, making them less likely to contaminate the surrounding environment [Lewińska et al., 2019].

The organic matter in compost can bind with metallic trace elements, forming complexes that are less likely to be leached or taken up by plants. This process is known as organic matter complexation [De Souza et al., 2019]. As composting

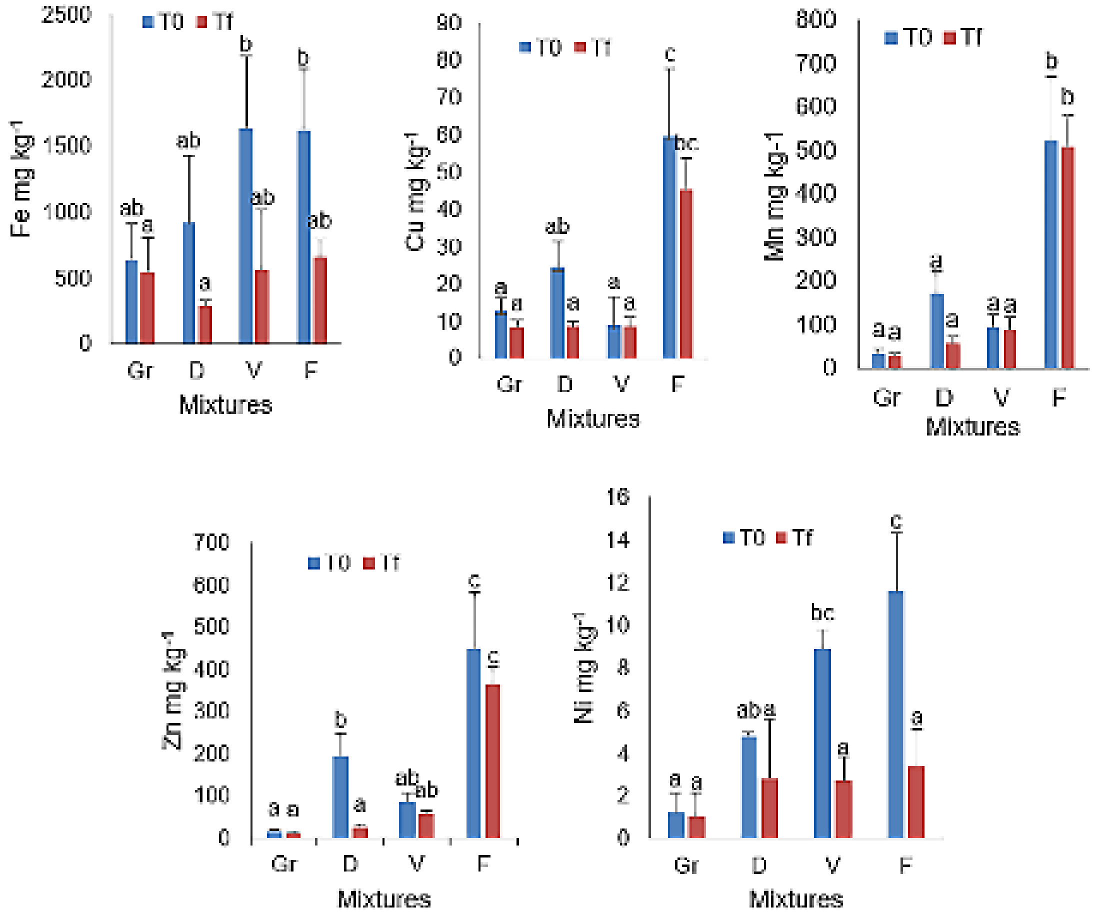

Figure 1. Initial and final TME contents (Fe, Cu, Mn, Zn and Ni) in various organic waste composts

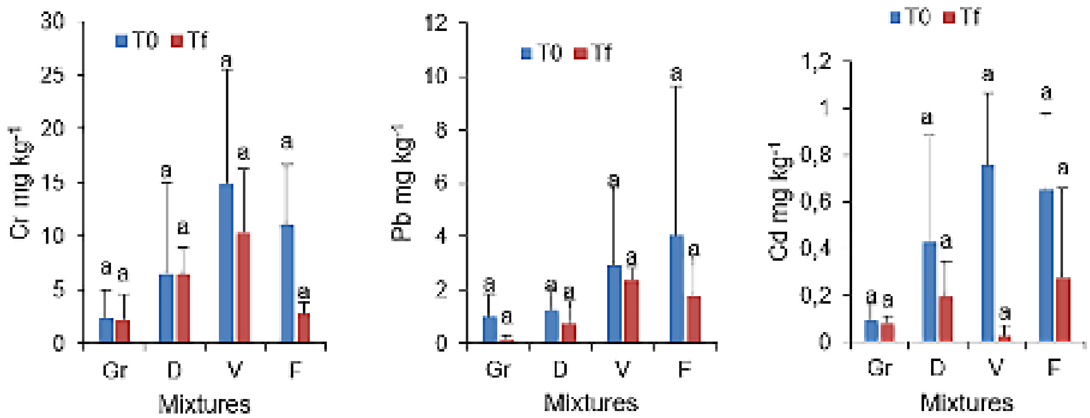

Figure 2. Initial and final levels of heavy metals (Cr, Pb and Cd) in various organic waste composts

involves the addition of a significant amount of organic material, the concentration of metallic trace elements in the final compost may be diluted, reducing their overall content [Saffari et al., 2020]. Some metallic trace elements can undergo volatilization during the composting process. This is particularly relevant for certain elements such as mercury, which can be transformed into volatile forms and released into the atmosphere [Guangbin et al., 2021].

Quality assessment of the 4 types of composts (olive pomace, organic household waste, green waste and poultry manure) revealed that the various composts showed a decrease in all trace metal elements concentrations at the end of the composting process.

Table 1. TME limit values [NF. U 44-051, 2006]

T.M.E	Gr (mg kg^{-1})	D (mg kg^{-1})	V (mg kg^{-1})	F (mg kg^{-1})	TME limit values (mg kg^{-1}) [NF. U 44-051, 2006]
As	-	-	-	-	18
Cd	0.08 ± 0.03	0.19 ± 0.16	0.025 ± 0.06	0.27 ± 0.42	3
Cr	2.22 ± 2.42	6.51 ± 2.51	10.40 ± 5.96	2.75 ± 1.19	120
Hg	-	-	-	-	2
Ni	1 ± 1.17	2.80 ± 2.82	2.68 ± 1.14	3.33 ± 1.80	60
Pb	0.1125 ± 0.19	0.75 ± 0.84	2.35 ± 0.50	1.74 ± 1.52	180
Se	-	-	-	-	12
Cu	8.30 ± 1.93	8.54 ± 1.22	8.46 ± 2.50	45.34 ± 8.43	300
Zn	10.88 ± 3.92	25.30 ± 7.08	58.57 ± 6.47	364.46 ± 41.22	600
Mn	28.85 ± 7.39	58.62 ± 16.66	91.45 ± 27.78	509.73 ± 72.57	-
Fe	545.18 ± 261.28	287.57 ± 44.58	561.68 ± 453.20	652.62 ± 151.77	-

Determining the bioavailability of metals in composts and the variations in their distribution generated by changes in physico-chemical properties during composting are important for the agronomic quality of the final product [Petruzzelli, 1989; Planquart et al., 1999; Hsu and Lo., 1999]. The contents of the olive pomace studied are close to those of pomace from a three-phase extraction system in Spain (Fe – 614 mg·kg^{-1}, (Zn – 21 mg·kg^{-1}, Cu – 17 mg·kg^{-1}). However, a lower value of (16 mg·kg^{-1}) was recorded for Manganese [Alburquerque et al., 2004]. Higher values were observed for olive pomace and poultry manure in Nikel before composting (55 mg·kg^{-1}, 49 mg·kg^{-1} respectively). Similarly, the Manganese concentration in olive pomace was lower than that found in Spain (56 mg·kg^{-1}), while in poultry manure it was much higher (322 mg·kg^{-1}) [Tortosa et al., 2012]. A Ni concentration of 0.1 mg·kg^{-1} appears to have a beneficial effect on the growth of isolated *L. leucocephala* roots, a depressive effect for the same plant from a concentration of 1 mg·kg^{-1}, and a lethal effect for a concentration of 10 mg·kg^{-1} [Verlière et al., 1981].

Chromium, and more specifically Cr (VI), is a highly toxic element. This toxicity has been demonstrated at various stages of plant growth and development [Shanker et al., 2005]. A higher level has been observed in olive pomace in Italy (15 mg·kg^{-1}) [Nasini et al., 2013]. Despite the high concentration of some elements, it remains below the regulatory thresholds set by the NFU 44-051 standard for organic soil improvers [NF. U 44-051: 2006]. Of course, variations in the chemical composition of macronutrients and micronutrients depend on a number of factors, including their variety, maturity stage and the physico-chemical characteristics of the soil [Alvar-Beltràn et al., 2021].

Canaruto et al., (1991) reported a reduction in soluble metal concentrations in mature municipal waste composts. Leita & De Nobili (1991) showed a large decrease in the soluble fraction of Pb and Zn during the first few days of composting municipal waste, which can be linked to the decomposition of soluble non-humic substances (polysaccharides, peptides and amino acids...) representing over 90% of the soluble carbon in this compost. Paré et al (1999) found that, during the co-composting of biosolids and municipal waste, the residual forms of certain metals (Zn, Cr, Cu and Pb) increased by 145%, 124%, 73.6% and 26.3% respectively. While Ni remains relatively constant and Co decreases by 60%. They observed that the decrease in the fractions of easily extractable and exchangeable metals (Cr, Ni, and Zn) is linked to an increase in the concentration of COO^- carboxyl groups. Thus, they suggest a decrease in metal extractability and exchangeability due to the association of metal ions with carboxylate groups in organic matter. Echab et al (1998) demonstrated that sludge treatment by composting has a significant effect on the decrease in the $CaCl_2$ extractable exchangeable fraction for elements such as Pb, Cu, Zn and Cd. These authors attributed these variations to the complexation of metals with neoformed humic substances. However, this distribution is reversible for certain metals such as Zn and Cd, which show an increase in extractability during compost maturation. Pb, Zn and Cr levels in palm stover and poultry manure composts from southwest Ivory Coast are below French standards. On the other hand, high levels of Cr and Zn were observed in the starting materials. This suggests that composting has reduced the metal content of the various composts [Gnimassoun et al., 2020].

The initial chromium (Cr), zinc (Zn) and plumb (Pb) contents of raw leaf and manure, the results indicate that the starting raw materials were high in Cr (450 $mg\cdot kg^{-1}$ for cob and 309 $mg\cdot kg^{-1}$ for poultry manure) and low in Pb and Zn (Pb – 15 $mg\cdot kg^{-1}$, Zn – 33 $mg\cdot kg^{-1}$ for leaf and Pb – 85.5 $mg\cdot kg^{-1}$ for manure). However, poultry manure has very high Zn levels compared with palm stalks (656 $mg\cdot kg^{-1}$). Comparison of initial and final contents shows a drop in elemental content during composting, with the exception of Pb and Zn, for which there is no variation with T0. This decrease increases with the amount of manure added in the different treatments, whatever the element, from T0 to T3. The percentage loss was 88.55 to 95.39%, 73.31 to 83% and 81.48 to 87.22% for Cr, Pb and Zn respectively [Gnimassoun et al., 2020]. Indeed, according to Pakou et al. (2009), composting reduces the availability of metals present in organic waste. According to Amir et al. (2005), during composting, TME levels tend to decrease through leaching following their release by decomposition of organic structures. Thus, soil amendment with compost can be beneficial for food crops. However, it should be carefully monitored, as repeated applications of compost could, through the accumulation of pollutants, have a disruptive effect on the biological functioning of soils [Houot et al., 2009].

In their study of the effects of different additives and aerobic composting factors on the reduction of heavy metal bioavailability and on compost parameters, Abdellah et al., (2022) show that the results revealed that additives significantly reduced heavy metal bioavailability by $\geq$ 40% in final compost products compared with controls. The bioavailability reduction rates were -40%, -60%, -57%, -55%, -42% and -44% for Zn, Pb, Ni, Cu, Cr and Cd. However, the escalation of additive quantities did not exhibit a statistically significant impact on reducing the bioavailability of heavy metals ($p > 0.05$). Notably, the utilization of zeolite as an additive, chicken manure as a raw material, sawdust as a blowing agent, and a reactor as the composting method demonstrated the most substantial reduction in heavy metal bioavailability ($p < 0.05$). The outcomes of this meta-analysis could contribute valuable insights for the selection, modification, and application of composting additives and factors to effectively manage the levels of heavy metal bioavailability in compost products [Abdellah et al., 2022].

Lin et al, (2021) demonstrated in their study of the simultaneous reduction of antibiotic and heavy metal pollution during manure composting, that residual concentrations of heavy metals and antibiotics in compost treated with attapulgite-activated carbon composite were 7% to 32% and 4% to 64% lower than in controls. The addition of attapulgite-activated carbon composite reduced enrichment of Cr, Cd, Pb and As during composting. Additionally, according to Hao et al. (2019), the inclusion of biochar and montmorillonite alone had a discernible effect on diminishing the bioavailability of heavy metals in the composting process of chicken manure. The findings indicated a significant reduction in Cu bioavailability by 90.3% and 81.2% and Zn by 11.7% and 15.6% for biochar and montmorillonite, respectively.

Physico-chemical analysis of compost produced from household waste in Butembo, eastern Democratic Republic of Congo, revealed low levels of trace metal elements in compost produced from household waste in Butembo. Most of these levels are below the recommended standards for good-quality compost (Cu – 116.2 $mg\cdot kg^{-1}$; Zn – 14.5 $mg\cdot kg^{-1}$; Pb – 0.03 $mg\cdot kg^{-1}$; Ni – 0.20 $mg\cdot kg^{-1}$; Cr – 0.005 $mg\cdot kg^{-1}$), while other elements, such as cadmium and mercury, are absent from the compost [Lwanga et al., 2023].

CONCLUSIONS

Ultimately, composting is an important step in the sustainable management of organic waste, helping to preserve environmental quality by reducing the risks associated with heavy metals and playing a significant role in their reduction in the environment, while improving soil fertility. The results of this analysis of heavy metals in these compost samples indicate that they comply with regulatory standards. They can be safely used as organic soil improvers to enrich agricultural soils and promote plant growth without the risk of excessive metal contamination. These results demonstrate the quality of the composting process used to produce these organic amendments and their suitability for environmentally-friendly agricultural use. However, it is advisable to continue monitoring compost quality on a regular basis to ensure their environmental safety and usefulness in soil improvement. This study validates and strengthens the findings of prior research on the organic solid waste valorization via composting. As a result to mitigate significant environmental risks by diminishing trace metal elements through this biological process. This method could be an effective solution to reduce the organic waste volume and minimize their environmental risks in terms of heavy metals.

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