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ENHANCED REMOVAL OF AROMATIC AMINO ACID FROM WATERS OF VARIABLE MINERALIZATION USING ALUMINUM SULFATE AND POWDERED ACTIVATED CARBON

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ABSTRACT

Aromatic amino acids are key constituents of dissolved organic nitrogen in natural and contaminated waters. Their presence in drinking water sources is of increasing concern due to their reactivity with disinfectants, leading to the formation of nitrogenous disinfection by-products (N-DBPs), which are often more toxic than carbon-based analogs. This study evaluates the removal of a representative aromatic amino acid, phenylalanine, using aluminum sulfate (AS) as a coagulant, both alone and in combination with powdered activated carbon (PAC), in water matrices exhibiting different levels of mineralization.

Jar-test experiments were conducted using distilled water and three Algerian groundwater samples characterized by increasing electrical conductivity and hardness. Coagulation with AS alone resulted in limited phenylalanine removal (18.66% to 30.09%), especially in mineralized waters. This low efficiency is attributed to phenylalanine's low polarity and zwitterionic nature, as well as to ionic interference with aluminum speciation and floc formation.

The addition of PAC significantly improved removal efficiency across all water types, achieving up to 87.2%. A consistent optimal PAC dose (70 mg/L) was observed regardless of mineralization level, indicating that adsorption is primarily governed by interactions between phenylalanine and the PAC surface. Among all samples, water with moderate mineralization exhibited the highest removal efficiency in the combined AS–PAC process, likely due to favourable conditions for both flocculation and adsorption.

These results demonstrate that conventional coagulation alone is insufficient for effective removal of low-polarity amino acids in mineralized waters. However, combining coagulation with adsorption provides a robust and scalable strategy for reducing aromatic

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amino acid concentrations, thereby limiting the formation of hazardous disinfection by-products in treated drinking water.

Keywords: Amino acid, Algerian water, Mineralization, Aluminum sulfate, Powdered activated carbon, Coagulation-flocculation, Mechanisms.

INTRODUCTION

Water resources are increasingly impacted by anthropogenic activities including industrial discharges, agricultural runoff, and rapid urban expansion. Climate change is profoundly altering the availability and quality of water resources worldwide (Nichane and Khelil, 2015; Nakou et al., 2023; Chadee et al., 2023), with increasing temperatures leading to accelerated evaporation, especially of lakes and reservoirs (Chibane and Ali-Rahmani, 2015; Hamimed et al., 2017; Boutoutaou et al., 2020).

These pressures contribute to the contamination of freshwater systems with organic, inorganic, and biological pollutants (Bacha and Achour, 2018). Organic matter in aquatic systems originates from both autochthonous sources, such as microbial and algal activity, and allochthonous inputs, including industrial synthetic compounds and naturally occurring organics from soil and rock (Thurman, 1985).

Natural organic matter (NOM) in water is a heterogeneous mixture that includes humic substances, amino acids, polysaccharides, peptides, lipids, and small organic acids (Frimmel, 1998; Varma et al., 2022). Its hydrophobic fraction is rich in aromatic carbon and conjugated systems, while the hydrophilic portion comprises aliphatic and nitrogenous compounds such as sugars, proteins, and amino acids (Feng et al., 2022; Pi et al., 2022). Amino acids are particularly important constituents of dissolved organic nitrogen (DON). Their free forms typically contribute about 5% of total organic nitrogen, while protein- and humic-bound amino acids can account for up to 40% (Guergazi and Achour, 2013). In natural waters, amino acid concentrations range from 50 to 1000 µg/L, contributing between 15% and 35% of DON and up to 2.6% of the dissolved organic carbon (Thurman, 1985; Dotson and Westerhoff, 2009).

Among amino acids, phenylalanine (Phe) is a nonpolar, hydrophobic compound widely used in food, pharmaceutical, and cosmetic industries, particularly in the synthesis of aspartame, a common artificial sweetener (Sakamoto, 2015; Perkowski and Warpeha, 2019). Its increasing presence in the environment raises concern, as it has been detected in surface and drinking waters at concentrations ranging from 0.30 to 5.19 µg/L (Zhai et al., 2021; Yang et al., 2020).

While no systematic monitoring data exist for amino acid concentrations in Algerian waters, localized studies have reported the presence of amino acids in surface waters in western Algeria, likely resulting from untreated wastewater discharge (Benkaddour et al., 2019). Moreover, humic substances with amino acid components have been identified in various Algerian dams, accounting for 60–90% of the total organic carbon content (Achour and Moussaoui, 1993; Achour et al., 2009). Since amino acids are often found in combined forms within humic or protein-like structures, it is reasonable to assume that they are present in significant concentrations in Algerian waters. It is now well known that these humic substances exhibit high aromaticity and chemical reactivity, particularly during chlorination (Johnson et al., 1982; Yang and Shang, 2004). This assumption is consistent with findings that link the formation of disinfection byproducts in Algerian surface waters to the reactivity of humic materials during chlorination. Indeed, several investigations (Achour and Guergazi, 2002; Achour et al., 2009; Achour and Chabbi, 2014) have shown that chlorination of Algerian surface waters containing humic substances can result in the formation of organohalogen compounds, especially trihalomethanes (THMs), which are known for their mutagenic and carcinogenic potential (Kalita et al., 2024; Cortés and Marcos, 2018).

Due to its aromatic ring and amino group, phenylalanine is particularly reactive with chlorine and other oxidants, forming a range of disinfection by-products (DBPs), including nitrogenous species such as haloacetonitriles and phenylacetonitrile (Hureiki et al., 1994; Freuze et al., 2004; Ma et al., 2016; Chen et al., 2024). DBPs derived from amino acids are especially concerning because nitrogenous DBPs (N-DBPs) tend to be more toxic than carbonaceous ones (Dotson and Westerhoff, 2009; Wagner and Plewa, 2017; Wu et al., 2020). Wang et al. (2023) demonstrated that the three aromatic amino acids—tyrosine, tryptophan, and phenylalanine—can form DBPs during chlorination, emphasizing the reactivity of DON as a key precursor to such compounds.

To mitigate DBP formation, it is necessary to reduce the levels of both hydrophilic and hydrophobic precursors in raw water. Conventional treatment processes such as coagulation-flocculation, adsorption, membrane filtration, and advanced oxidation show variable efficiencies for removing organic micropollutants like amino acids (Saxena et al., 2018; Guminska and Klos, 2020; Peters et al; 2021; Zhu et al., 2023). Coagulation-flocculation, though widely used and cost-effective, is generally less efficient for small, nonpolar molecules such as phenylalanine (Dotson and Westerhoff, 2009; Matilainen et al., 2010). Activated carbon, particularly in powdered form (PAC), is a promising supplement due to its high surface area and affinity for hydrophobic organics (Bouchemal and Achour, 2007; Youcef et al., 2014; Yimiam et al., 2017; Harrat and Achour, 2016).

The efficiency of coagulation and flocculation processes is influenced by several factors such as coagulant dose and pH (Lefebvre and Legube, 1990; Achour and Guesbaya, 2005; Saxena et al., 2018). Water composition also plays a critical role in removal efficiency of organic contaminants. High salinity and hardness, common in southern Algerian waters, can interfere with coagulant performance (Hecini and Achour, 2014; Bacha and Achour, 2017; Bacha and Achour, 2023)

Given this context, the present study aims to evaluate the effectiveness of phenylalanine removal from waters of varying mineralization using aluminum sulfate (AS) alone and in combination with powdered activated carbon (PAC). Phenylalanine is considered both a model compound for DBP precursors and a representative of low-polarity, low-molecular-weight organics that are difficult to remove via conventional coagulation. The study focuses on identifying optimal conditions, including reagent dosages, and investigating the influence of water mineralization on removal efficiency. Special attention is given to understanding the synergistic mechanisms involved in the combined

AS/PAC treatment, with the goal of proposing an integrated and scalable solution for improving drinking water quality in inorganic-rich environments.

MATERIAL AND METHODS

Preparation of reagents

In all coagulation-flocculation experiments, aluminum sulfate ($Al_2(SO_4)_3.18\ H_2O$) served as the coagulant. A stock solution is prepared by dissolving 10 grams per liter of this reagent in distilled water.

Powdered activated carbon (PAC), with a specific surface area of 658 m^2/g and a particle size of 20 µm, is the adsorbent utilized.

Preparation of phenylalanine solutions

Phenylalanine, abbreviated by the symbol “Phe”, is an essential α-amino acid. This amino acid is categorized as neutral and nonpolar due to the inert and hydrophobic characteristics of its benzyl side chain. In our study, the amino acid under consideration (phenylalanine) is a Sigma-Aldrich compound of high chemical purity. The key physicochemical characteristics of phenylalanine are outlined in Table 1.

To prepare phenylalanine solutions, the compound is dissolved in distilled water or groundwater that exhibits different mineralization levels. Groundwater is sourced from drilling waters in the Biskra region of South East Algeria. The stock solution is prepared at a concentration of 400 mg/L, from which further dilutions are made for both calibration and jar testing. Distilled water has a pH range of 6.07 to 6.79 and a conductivity of 2 to 5 µs/cm, while the chemical composition of the three types of groundwater (Drouh, Wadi El Hai, Camping) is detailed in Table 2. The measured parameters were determined using standard analysis methods (APHA, 2005).

Table 1: Characteristics of phenylalanine (O’Neil, 2001; Sprenger, 2007)

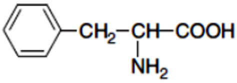
Current name	Phenylalanine
Chemical name	2-Amino-3-phenylpropanoic acid
Chemical structure	
Molecular formula	$C_9H_{11}NO_2$
Molar mass ($g.mol^{-1}$)	165.19
pK –COOH	1.83
pK $–NH_3^+$	9.13
Isoelectric Point	5.48
Purity %	99
Solubility in water	27.9 g/L at 25°C

Table 2: Physicochemical parameters of mineralized water from Biskra boreholes

Parameters	Groundwater samples		
	Drouh	**Wadi El Hai**	**Camping**
Temperature (°C)	16.5	18.5	17
pH	7.88	7.6	7.6
Total Hardness (TH) (mg $CaCO_3$/L)	656	752	1368
Alkalinity (mg $CaCO_3$/L)	160	156	196
Cl^- (mg/L)	94.6	1100	2440
SO_4^{2-}(mg/L)	332	440	592
NO_3^- (mg/L)	8.4	9.5	33.5
Na^+ (mg/L)	45.2	468.3	846.3
K^+ (mg/L)	2.03	5.03	13.22
PO_4^{3-}(mg/L)	0.3	0.1	0.6
Electrical Conductivity EC (mS.cm^{-1})	1.02	2.45	4.29

Phenylalanine analysis

The residual concentrations of the organic compound examined were determined via UV spectrophotometry, employing UV absorbance calibration curves that relate to the initial concentrations of phenylalanine (C_0). Fig. 1 presents the calibration curves that plot (UV absorbance=y) against the initial concentrations ($x=C_0$) of phenylalanine solutions at a wavelength λ = 257 nm.

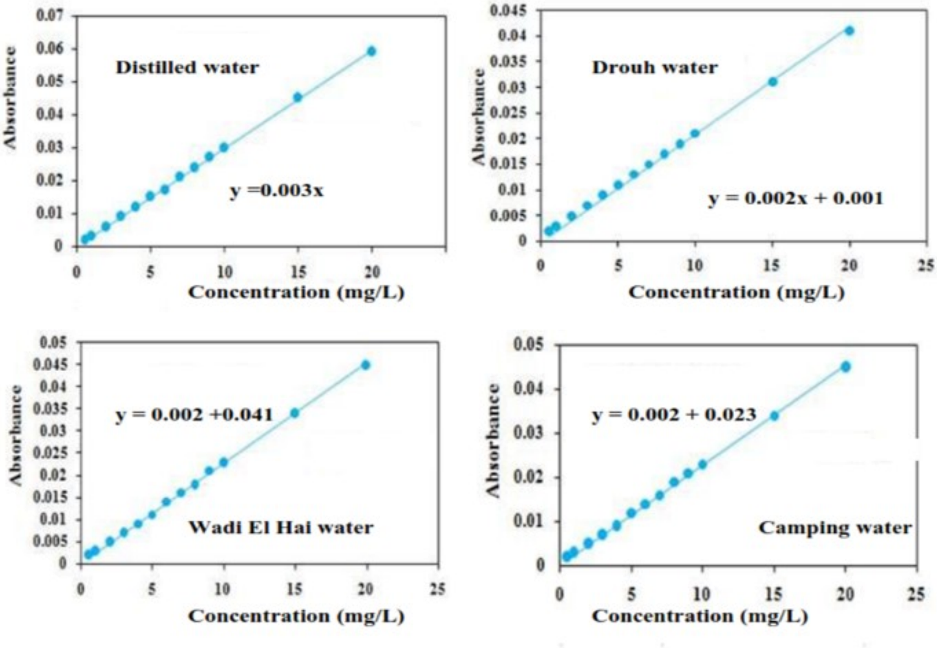


Figure 1: Calibration curves of phenylalanine in various mineralized waters

The application of the least squares method to the corresponding values of UV absorbance and initial phenylalanine concentration resulted in a linear relationship, which exhibited excellent coefficients of correlation ($0.99<R^2< 1$). It is important to highlight that this relationship is dependent on the medium utilized for the dilution of the amino acid.

Test of coagulation-flocculation

The coagulation-flocculation of phenylalanine was carried out in accordance with the jar-test analytical procedure. The equipment used consists of a flocculator with six stirrers (Fisher 1198 Flocculator), with a rotational speed that can be varied from zero to 200 rpm, in order to simulate the dynamics of the coagulation-flocculation process. This apparatus allows for the simultaneous stirring of the solutions contained in a series of 500 ml beakers. Note that each sample was agitated at the speed of 200 rpm for a period of 2 minutes after the addition of the coagulant. Afterwards, the speed was reduced to 60 rpm for a 30 minutes flocculation period. Finally, the flocs were allowed to settle for 30 minutes, before filtration through a 0.45 µm cellulose membrane.

The utilization of activated carbon alongside aluminum sulfate necessitates the centrifugation of the supernatant at a speed of 3000 rpm for a duration of one hour to enhance the separation process.

After the samples were extracted, they underwent analysis via UV spectrophotometry. The efficiency of removal (E%) for the tested organic compound was calculated according to the formula:

$$E(\%) = \frac{C_0 - C_f}{C_0} \times 100 \tag{1}$$

where C_0 denotes the initial concentration of phenylalanine prior to the addition of the coagulant, and C_f represents the final concentration of this organic compound post-treatment.

RESULTS AND DISCUSSION

Effect of water mineralization on the coagulation-flocculation of phenylalanine using aluminum sulfate

A concentration of 10 mg/L of phenylalanine was dissolved in several water types, specifically distilled water and borehole water. The mineralization levels of these waters are progressively higher, as indicated by the recorded values of electrical conductivity and total hardness. Since the groundwater is sufficiently buffered, there was no need for pH modification. During this testing phase, the solutions prepared were subjected to coagulation using varying quantities of aluminum sulfate.

In Fig. 2, the findings related to the changes in elimination yields (E%) of phenylalanine in response to increasing coagulant dosage are depicted. This visual representation enables a comparative evaluation of the results among different dilution waters. Furthermore, Table 3 serves to summarize the operational conditions pertinent to the coagulation-flocculation process, with the objective of maximizing the elimination of phenylalanine.

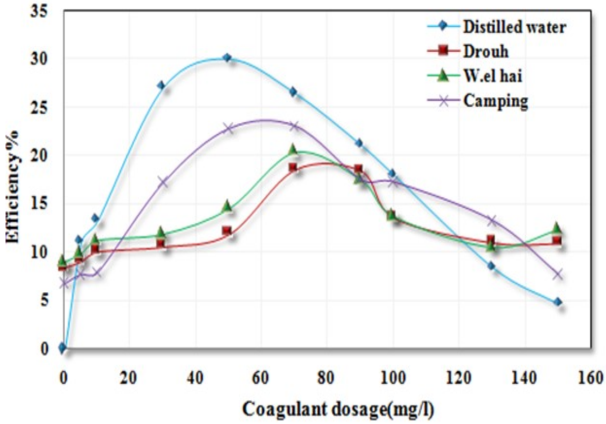


Figure 2: Impact of water mineralization on the efficiency of phenylalanine removal through escalating doses of aluminum sulfate

The experimental results displayed in Fig. 2 and Table 3 clearly demonstrate that the efficiency of phenylalanine (Phe) removal by coagulation-flocculation using aluminum sulfate ($Al_2(SO_4)_3 \cdot 18H_2O$) is highly sensitive to the mineralization of the water in which the amino acid is dissolved.

While phenylalanine removal in distilled water peaked at ~30% with a coagulant dose of 40 mg/L, the removal efficiency decreased in mineralized waters despite increasing coagulant dosages—falling to 18.66% in Drouh, 20.44% in Wadi El Hai, and 22.88% in Camping water, even at coagulant doses as high as 90 mg/L.

Table 3: Optimal results for the removal of phenylalanine (C_0 =10mg/L) from various mineralized water sources. D_{opt}: Optimal dose of aluminum sulfate; E_{opt}: optimal removal efficiency

Water samples							
Distilled water		Drouh water		Wadi El Hai water		Camping water	
pH =7 EC=5.10^{-3} mS/cm		pH = 7.88 EC= 1.2 mS /cm		pH =7.6 EC=2.45 mS /cm		pH =7.6 EC =4.29 mS /cm	
D_{opt} (mg/L)	E_{opt} (%)	D_{opt} (mg/L)	E_{opt} (%)	D_{opt} (mg/L)	E_{opt} (%)	D_{opt} (mg/L)	E_{opt} (%)
40	30.09	60	18.66	70	20.44	90	22.88

Phenylalanine behavior in aqueous media

Phenylalanine is a neutral, nonpolar aromatic amino acid, with a benzyl side chain that imparts hydrophobicity and limits its interaction with hydrophilic coagulant species. At pH values near its isoelectric point (pI = 5.48), phenylalanine exists predominantly in its zwitterionic form, featuring a negatively charged carboxylate group ($–COO^-$) and a positively charged protonated amine group ($–NH_3^+$). In the tested waters (pH 7–7.88), phenylalanine remains mostly zwitterionic, but the carboxyl group is fully deprotonated, which favors some electrostatic interactions with aluminum-hydrolyzed species, although this is weakened by the amino acid's low polarity.

Another notable observation is the non-monotonic trend in removal efficiency with increasing aluminum sulfate dose. In all cases, phenylalanine removal improves up to an optimal dose, after which it declines. This contrasts with the behavior of larger, more complex organics like humic substances, for which the removal efficiency typically stabilizes after reaching an optimum (Achour and Guesbaya, 2006; Bacha and Achour, 2023).

This drop in efficiency beyond the optimum can be attributed to several interrelated mechanisms:

- Charge reversal: Excess aluminum ions can overcompensate surface charges, causing restabilization of colloids and dispersion of aggregates due to positive ζ-potential (Bottero and Lartiges, 1993).
- Microsolubilization: High coagulant concentrations may generate excess amorphous $Al(OH)_3$ particles, which trap water molecules and reduce interaction with target organics (Matilainen et al., 2010).
- Saturation and steric hindrance: Phenylalanine, being a small zwitterionic molecule, has limited binding sites. Once interactions with Al species (e.g., through amino or carboxyl groups, or π–π interactions) are saturated, further aluminum addition does not improve removal and may hinder floc growth by crowding or altering surface chemistry.

Coagulant chemistry and reaction mechanisms

Aluminum sulfate dissociates to yield Al^{3+} ions, which undergo hydrolysis depending on pH to form a variety of aluminum hydroxo-species ($Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_3(s)$, $Al(OH)_4^-$). At the slightly basic pH of the groundwater samples (7.6–7.88), $Al(OH)_3$ precipitate formation is dominant. This amorphous floc can remove organic molecules via (Edzwald and Van Benschoten, 1990, Achour and Guesbaya, 2005; Bacha and Achour, 2023):

- Charge neutralization: destabilizing charged colloids.
- Sweep flocculation: enmeshment of dissolved compounds in the settling floc.

- Ligand exchange and complexation: direct interaction between Al^{3+} species and functional groups of the target molecule.

However, due to phenylalanine's low polarity and lack of multiple reactive functional groups (compared to polyphenolic or humic compounds), it exhibits low affinity for hydrolyzed aluminum species. This explains the moderate removal efficiency even at optimized coagulant doses.

Influence of water mineralization

The increasing electrical conductivity (EC) and hardness across the waters tested (from 0.005 mS/cm in distilled water to 4.29 mS/cm in Camping water) reflect rising levels of Ca^{2+}, Mg^{2+}, Na^{+}, Cl^{-}, SO_4^{2-}, and HCO_3^{-}. These ions affect the process in several ways. Table 4 summarizes the main hypotheses concerning the reaction mechanisms during these first tests.

Table 4: Mechanistic Summary and Chemical Rationale

Water Type	Key Chemical Conditions	Mechanism Impact	Phe Removal Efficiency (Eopt)
Distilled	Low ionic strength, pH ~7	Favorable Al^{3+} hydrolysis, minimal interference. Weak but clean floc formation with minor electrostatic interaction with Phe zwitterions.	30.09%
Drouh	Moderate hardness, pH 7.88	Buffered pH near optimal for $Al(OH)_3$ precipitation. Moderate sweep flocculation. Ca^{2+} aids floc formation.	18.66%
Wadi El Hai	High Na^{+} and Cl^{-}, EC ↑	Ionic strength compresses double layer; Al^{3+} competes with background ions. Reduced complexation with Phe.	20.44%
Camping	Very high mineralization, EC 4.29 mS/cm	Aluminum speciation shifts towards soluble forms. Na^{+}, SO_4^{2-}, and Cl^{-} interfere with Phe binding.	22.88%

- Ionic strength compresses the electrical double layer of colloids and particles, promoting faster aggregation of flocs (Bottero and Lartiges, 1993). Yet, in the case of small, hydrophobic molecules like phenylalanine, this aggregation does not significantly enhance removal, as they are poorly associated with colloidal surfaces.
- Bicarbonate and carbonate ions act as buffers but can also interfere with coagulant hydrolysis, promoting the formation of soluble complexes like $Al(OH)_4^{-}$ at high pH, which are ineffective for sweep flocculation.

- High chloride and sulfate levels, especially in Wadi El Hai and Camping waters, may compete with phenylalanine for binding with aluminum species, reducing complexation efficiency.
- Sodium and calcium ions, especially at high concentrations (Na^+ > 800 mg/L in Camping water), can further destabilize weak interactions between aluminum flocs and phenylalanine by increasing solvation and dispersion of hydrophobic organics.

Comparison with other studies and molecules

Compared to humic substances or polyphenols, phenylalanine is structurally simpler, less reactive, and poorly adsorbed onto flocs, resulting in inferior removal performance.

Zhou et al. (2017) and Edzwald & Van Benschoten (1990) demonstrated that high Ca^{2+} concentrations improve coagulation of natural organic matter by forming bridges between functional groups and coagulant species. However, in phenylalanine's case, this effect is marginal due to the lack of multiple coordination sites. Studies by Achour and Guesbaya (2006), Hecini, and Achour (2014) also affirm that saline environments can either improve or hinder coagulation depending on the organic compound's reactivity—highlighting the unique challenge posed by non-reactive, hydrophobic, low-molecular-weight molecules like phenylalanine.

Similar trends have been observed for tyrosine (Tyr) and tryptophan (Trp), other aromatic amino acids with limited removal during coagulation in low ionic strength water (Dotson & Westerhoff, 2009; Hureiki et al., 1994). However, tyrosine exhibits higher removal rates than phenylalanine when treated with aluminum- or iron-based coagulants. It's due to its additional hydroxyl group increasing electrostatic and hydrogen bonding interactions （Chen et al., 2024; Wu et al., 2020. Tryptophan removal can also exceed that of phenylalanine due to strong π–π stacking and possible coordination between the indole ring and metal centers (Lu et al., 2021).

In terms of disinfection by-product (DBP) formation, tryptophan and tyrosine are more reactive than phenylalanine, often producing higher yields of N-DBPs, especially haloacetonitriles and haloacetamides, due to their nitrogen-rich structures (Wang et al., 2023). Thus, while phenylalanine serves as a conservative model for studying DBP precursor behavior and coagulation response, its lower polarity and minimal functionality make it a less reactive but more difficult target for conventional coagulation compared to Tyr and Trp.

All these findings stress the necessity for advanced or complementary treatment methods—such as adsorption with powdered activated carbon—to ensure effective removal of phenylalanine and similar hydrophobic microcontaminants in mineralized waters.

Phenylalanine removal from waters of varying mineralization using a combined aluminum sulfate and activated carbon treatment

During this phase of the study, the experiments involved performing coagulation-flocculation of phenylalanine using aluminum sulfate in combination with powdered activated carbon. This adsorbent material was used here as a flocculation aid at increasing doses for an optimal coagulant dose. The dilution waters used were still distilled water, Drouh water, Wadi El Hai water, and Camping water. The results are presented in Fig. 3 and summarized in Table 5.

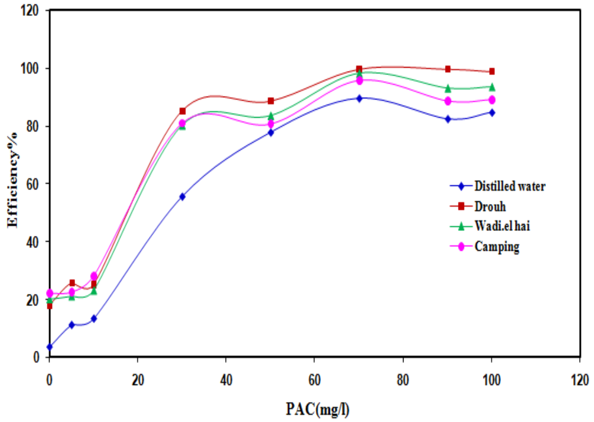


Figure 3: Impact of PAC dosage on the efficiency of phenylalanine (C_0 =10mg/L) removal in different mineralized water samples.

Table 5: Optimal results of phenylanine removal by aluminum sulfate (AS) and activated carbon (PAC)

Water Type	AS alone Eopt (%)	AS + PAC Eopt (%)	AS Dose (mg/L)	PAC Dose (mg/L)
Distilled	30.09	74.6	40	70
Drouh	18.66	87.2	60	70
Wadi El Hai	20.44	80.4	70	70
Camping	22.88	76.9	90	70

The combined use of aluminum sulfate (AS) and powdered activated carbon (PAC) was found to markedly enhance the removal of phenylalanine (Phe) in all tested waters, irrespective of their mineralization levels. As shown in Figure 3 and Table 5 of the study, the addition of PAC to the optimal dose of coagulant significantly improved the elimination yields. For example, in distilled water, the removal efficiency increased from approximately 30% with AS alone to over 74% with the addition of PAC. Similar enhancements were observed in mineralized waters: in Drouh water, the efficiency rose from 18.66% to 87.2%; in Wadi El Hai, from 20.44% to 80.4%; and in Camping water, from 22.88% to 76.9%.

These results clearly demonstrate the effectiveness of PAC in adsorbing phenylalanine, especially in waters where the coagulation process alone is insufficient. Interestingly, the optimal dose of PAC (70 mg/L) was consistent across all types of water, despite their varying degrees of salinity and mineral content. This consistency suggests that the PAC's adsorption behavior is primarily influenced by the nature of the organic compound (phenylalanine) and its concentration, rather than by the ionic composition of the water.

Comparison with the use of coagulant alone

Fig. 4 shows a comparison of phenylalanine removal efficiencies by aluminum sulfate alone (AS) and by the coagulant (AS)/powdered activated carbon (PAC) combination.

When comparing these results with those obtained using aluminum sulfate alone, the benefits of adding PAC become even more apparent. In all water types, PAC addition more than doubled the removal efficiency. This contrast underlines the limitations of traditional coagulation-flocculation methods for removing small, hydrophobic organic molecules like phenylalanine. While aluminum sulfate remains effective for larger, more reactive compounds such as humic substances or polyphenols, it struggles with simpler molecules that offer few functional groups for complexation or surface attachment.

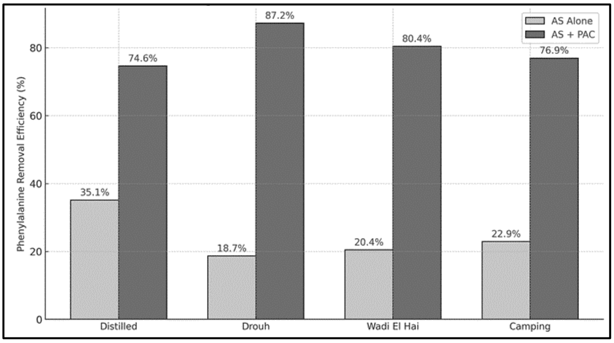


Figure 4: Phenylalanine removal from waters of varying mineralization using aluminium sulphate alone and in combination with PAC

Mechanisms Involved in the Enhanced Removal

The improvement observed with the AS/PAC combination can be attributed to the distinct yet complementary mechanisms of the two agents. Aluminum sulfate, through hydrolysis at near-neutral to slightly alkaline pH levels, generates amorphous aluminum hydroxide precipitates [$Al(OH)_3$] that can enmesh organic molecules via sweep flocculation (Edzwald and Van Benschoten, 1990). However, phenylalanine, due to its low polarity and zwitterionic nature, interacts only weakly with these flocs, limiting the overall efficiency of the coagulation process.

In contrast, PAC offers a hydrophobic surface that facilitates strong interactions with the aromatic side chain of phenylalanine via π–π stacking and Van der Waals forces. These interactions are largely independent of the presence of dissolved salts and enable PAC to serve as both an adsorbent and a flocculation aid, especially for small, nonpolar organic molecules like phenylalanine. The synergy between aluminum sulfate and PAC is particularly beneficial: the coagulant initiates the aggregation of particles, while PAC enhances the capture and retention of otherwise poorly reactive molecules.

Another notable observation is that the optimal dose of PAC required to achieve maximal phenylalanine removal was the same (70 mg/L) across all water types. This consistency suggests that PAC's adsorption capacity for phenylalanine reaches a plateau at this dose, beyond which no significant improvement is observed. Given phenylalanine's low molecular weight and specific aromatic structure, this dose likely corresponds to saturation of available active sites on the PAC surface. Additionally, since PAC is relatively inert to ionic interference, the adsorption process is not significantly altered by the mineral composition of the water.

Influence of water mineralization

An intriguing result emerges when comparing the performance of the AS/PAC combination across the different types of water. While more highly mineralized waters such as Camping and Wadi El Hai had previously shown slightly better performance under coagulation alone, the addition of PAC reversed this trend. Drouh water, characterized by moderate mineralization, produced the best removal efficiency with the combined treatment.

This reversal is chemically significant. In coagulation alone, inorganic ions such as Ca^{2+} and Mg^{2+} may assist in floc formation, improving the process slightly. However, high concentrations of Na^{+}, Cl^{-}, and SO_4^{2-} in highly mineralized waters can interfere with both aluminum hydrolysis and the adsorption process (Achour and Guesbaya, 2006; Bacha and Achour, 2017).

These ions compete with phenylalanine for available adsorption sites and can modify the surface properties of PAC, thereby reducing its efficiency. Additionally, in waters with elevated salinity, phenylalanine's solubility may increase, further reducing the molecule’s tendency to interact with PAC. Drouh water appears to represent a balanced environment where PAC adsorption can occur effectively without the inhibitory effects of high salinity. Its moderate buffering capacity also maintains favorable pH conditions for aluminum sulfate hydrolysis, resulting in optimal flocculation without excessive competition from background ions.

CONCLUSION

This study aimed to evaluate the efficiency of phenylalanine removal from waters of varying mineralization using aluminum sulfate (AS) alone and in combination with powdered activated carbon (PAC). The investigation focused on the effects of water composition, coagulant and adsorbent doses, and the interaction mechanisms between phenylalanine and the treatment agents.

Initial results showed that aluminum sulfate alone was insufficient for removing phenylalanine, particularly in mineralized waters, with removal efficiencies only slightly exceeding 30%. This limited performance is mainly due to phenylalanine's small molecular size, low polarity, and zwitterionic nature, which reduce its interaction with hydrolyzed aluminum species. Additionally, the presence of high concentrations of inorganic salts, such as sodium, sulfate and chloride, interfered with the flocculation process by altering aluminum speciation and competing with phenylalanine for available binding sites.

In contrast, the addition of powdered activated carbon significantly enhanced removal efficiencies across all water types, reaching up to 87% in moderately mineralized water (Drouh). PAC improved the process by providing hydrophobic and aromatic surfaces favorable to π–π stacking and adsorption interactions with phenylalanine. A key finding was that the optimal PAC dose (70 mg/L) remained constant regardless of water mineralization, indicating a surface saturation phenomenon rather than a matrix-dependent behaviour.

The combined AS/PAC treatment led to a reversal in the performance order of the tested waters. While distilled water showed the highest removal under AS alone, Drouh water became the most effective matrix under the combined treatment. This indicates that moderate mineralization may provide optimal conditions for both floc formation and adsorption, whereas highly mineralized waters introduce competitive effects that can reduce treatment efficiency.

These findings highlight the limitations of conventional treatment for hydrophobic, low-reactivity compounds and the value of combining adsorption and coagulation strategies.

Furthermore, PAC treatment reduces the concentration of aromatic amino acids like phenylalanine, which are known precursors to nitrogenous disinfection by-products (N-DBPs) such as phenylacetonitrile and haloacetonitriles. Therefore, the use of PAC not only enhances removal efficiency but also mitigates the formation of hazardous DBPs in downstream disinfection processes.

Future work should examine the application of this combined approach to other amino acids and organic micropollutants, as well as its scalability for real-world water treatment systems.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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