Assessing the effect of inorganic anions on TiO_2-photocatalysis and ozone oxidation treatment efficiencies

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Abstract: Considering the application of AOPs might be limited for the treatment of industrial wastewater with high inorganic load, and that partial results reported to date regarding this particular are inconclusive, even opposite in some cases, the effect of inorganic anions on the oxidation efficiency of photocatalysis and ozonation has been further assessed with statistical significance. While the presence of sulphate and chloride did not appreciably affect the photocatalytic oxidation of phenol, nitrate significantly enhanced the removal of COD (≈ 8-15%). The addition of carbonate simply increased the pH, which strongly inhibited the photocatalytic process; whereas if pH=5 was kept constant, the reduction of the COD was not affected by the presence of carbonate. On the other hand, sulphate, chloride and nitrate did not significantly affect the degradation of phenol by ozonation; whereas the presence of carbonate apparently enhanced the reduction of COD. It is actually proved that this improvement in the efficiency of the treatment was produced by the pH buffering effect of these ions, rather than to its presence itself, which actually significantly reduced the removal of COD (5-10%) by radical scavenging action in comparison to when the treatment was performed in the absence of anions in the solution adjusting the pH to similar basic values (≈9.5-13.5). When ozonation was performed at a pH close to neutral (6.5 ± 0.2) or basic (12 ± 0.2), at which the indirect oxidation of hydroxyl radical is surely widely active, the results were significantly enhanced in any case (COD removal ≈ 70-75%), whether in the absence or the presence of these anions; despite the significant slight radical scavenging effect (COD removal ≈ 65-70%) that was attributed to the addition of carbonate.

Key-words: photocatalysis; ozonation; radical scavengers; carbonate; sulphate; nitrate; chloride

Introduction

Advanced oxidation processes (AOPs) involving *in situ* generation of highly reactive transitory species like H_2O_2, $OH\cdot$, O_3, $O_2^{-}\cdot$ are applied when conventional wastewater treatment techniques become insufficient to treat persistent contaminants (1-3). Particularly, ozonation and photocatalytic oxidation with semiconductor catalysts, typically TiO_2, have been widely assessed and applied at industrial scale for this purpose (4-7).

Inorganic anions have been identified to reduce the efficiency of different AOPs (8-10), but actual comparison of their effect at different ion concentration values has been poorly assessed. In general, the produced loss of treatment efficiency attributed to the presence of inorganic anions has been explained by the scavenging effect of reactive radical ionic species and the generation of other by-radicals with weaker oxidation potentials (11-14). For example, chloride (Cl^{-}) has been addressed to scavenge hydroxyl radicals producing hydroxide and chlorine radical (15-17). Moreover, Cl^{-} may generate additional "hole"-scavenging in photocatalytic processes.

Similar inhibition mechanisms have been also attributed to other anionic species with a significant presence in wastewater, like sulphate (SO_4^{2-}) and nitrate (NO_3^{-}) (16-18); although other authors have addressed an insignificant effect of Cl^{-}, SO_4^{2-}, and NO_3^{-} on the efficiency of TiO_2-photocatalysis (19, 20). In addition, several authors have reported an improved oxidation efficiency of several AOPs caused by the strong oxidation potential of $SO_4\cdot^{-}$ radical itself (10, 21-24).

Besides radical scavenging, some anions (e.g. NO_3^{-}, SO_4^{2-}) may raise the turbidity of the solution, which causes the screening of UV radiation when applying photocatalytic treatments (10, 22); and the competitive adsorption of inorganic anions has been also proposed as an additional potential mechanism of inhibition, "stealing" surface active sites from organic molecules (10, 16, 25). Nevertheless, Wang *et al.* (26) observed no significant relationship between adsorption inhibition and photodegradation rate, attributing all the observed oxidation loss to the radical scavenging action exerted by NO_3^{-}, Cl^{-} and SO_4^{2-}. In addition, the competitive adsorption of anions is unlikely to occur under basic conditions because the amphoteric nature of TiO_2 will lead to the repulsion of negative electrostatic forces (22, 27, 28). Particularly, Epling and Lin (29) observed that photo-bleaching of anionic dyes was partially inhibited in the presence of HNO_3 and $NaHCO_3$, while it was accelerated for cationic ones.

Finally, most research assessing the effect of the presence of inorganic anions on the performance of ozone oxidation has been devoted to bicarbonate (HCO_3^{-}) and carbonate (CO_3^{3-}) action scavenging $OH\cdot$ radical (30-33):

$$CO_3^{2-} + OH\cdot \rightarrow CO_3^{3-} + OH^{-} \tag{1}$$

$$HCO_3^{-} + OH\cdot \rightarrow HCO_3\cdot + OH^{-} \tag{2}$$

$$HCO_3^{-} + OH\cdot \rightarrow CO_3\cdot^{-} + H_2O \tag{3}$$

In fact, Chiang *et al.* (33) used HCO_3^{-} and CO_3^{2-} to scavenge $OH\cdot$ radical in order to study direct oxidation by molecular ozone; and Song *et al.* (35) justified the reduced mineralization of CI Reactive Yellow 145 by ozone oxidation at pH>11.0 by the radical scavenging effect of HCO_3^{-}/CO_3^{2-} ions. On the other hand, Lair *et al.* (36) found that the presence of HCO_3^{-}/CO_3^{2-} inhibited the degradation of naphthalene by photocatalysis; but HCO_3^{-} has been reported to produce a negligible effect on the photocatalytic oxidation of Acid Orange 7 (26) and TNT (37).

In short, several authors have previously assessed in part the effect of inorganic anions on the degradation efficiency of several AOPs, although the reported results are inconsistent and have not been analyzed in terms of statistical significance. Therefore, the main objective of this essay aims to further assess the significance of the effect the most common anions present in industrial wastewater (SO_4^{2-}, Cl^{-}, NO_3^{-} and CO_3^{2-}) have on the treatment efficiency of phenol by ozonation and TiO_2-photocatalysis. These treatments were selected because they are AOPs widely applied with success in several industrial applications (4-7); while phenol was chosen because it is a commonly used model compound for the assessment of AOPs, and its nature and behaviour have been widely described when it is treated by ozonation or TiO_2-photocatalysis (1, 22, 38-43).

Experimental and methods

Materials

All used chemicals were analytical grade, provided by PANREAC S.A. (Barcelona, Spain). Phenol was available in its purest form (99.99%) and diluted with ultra-pure deionized water to the concentration of 200 mg·L^{-1} prior to experiment performance (initial COD=480 mg·L^{-1}). One of the inorganic anions selected to perform this essay (SO_4^{2-}, Cl^-, NO_3^- or CO_3^{2-}) was then added to the solution as the corresponding sodium salt at one of the following concentrations: 250, 500, 1000, and 2000 mg·L^{-1}. Every experiment was repeated 3-6 times to minimize the standard deviation of the results.

UV/TiO$_2$ oxidation

Aeroxide® TiO_2 P25 (Evonik, Essen, Germany) photocatalyst, with a specific surface area of 50 ± 15 m^2·g^{-1} and an average primary particle size of 21 nm, was first added to the solution at the concentration of 5 g·L^{-1}. This optimum TiO_2 dosage resulted from preliminary trials performed using catalyst concentration values ranging from 1 g·L^{-1} to 10 g·L^{-1}; and has been previously reported to produce optimal results in the treatment of industrial wastewater (44-46).

The oxidation treatment was carried out in a magnetically-stirred and specially shaped glass reactor (3 L) provided with the necessary ports in the upper part to insert pH and redox potential probes, which furthermore made possible the withdrawal of 5-ml aliquots from the reacting suspension for monitoring the evolution of the COD. The source of UV irradiation was a vertically located medium-pressure mercury vapour lamp (450 W; model 7825-34, ACE Glass Inc., Vineland, NJ, USA), inserted in a quartz cooling jacket, which radiates a total light power of 175.8 W covering from the infrared to the far ultraviolet wavelength regions. The whole assembly was placed in a photochemical safety cabin assisted with a cooling system. The treated solution was 2 L, and every experimental run was conducted for 2 hours. The photocatalyst was immediately separated from every collected sample by means of a 0.45 µm-pore filter at 15, 30, 45, 60, 90, and 120 min from the beginning of the treatment.

In the absence of inorganic anions, and when SO_4^{2-}, Cl^- and NO_3^- ions were added to the solution, the initial pH after the addition of the catalyst was approximately 5.0, and decreased thereafter to approximately 4.0 along the initial 30 min of reaction; keeping this value constant until the end of the experiment. The addition of Na_2CO_3 caused the initial pH to rise to about 10.0 to 12.0, depending on the added salt concentration, and was kept buffered by the presence of HCO_3^-/CO_3^{2-} ions. Therefore, additional experiments were carried out for testing the effect of pH alone: a) continuously adjusting pH to 5.0 (± 0.2) and 4.0 (± 0.2) after the addition of Na_2CO_3; and b) keeping pH=12.0 (± 0.2) when treating phenol in the absence of anions. pH was adjusted to acid values adding 1M H_2SO_4, as the effect of SO_4^{2-} was first checked to be non significative on the performance of the treatment; whereas 1N NaOH was added to perform the experiments keeping basic pH values.

Ozonation

Ozonation experiments were conducted in a glass jacketed cylindrical bubble reactor (height=1 m, diameter=5 cm) with a continuous feed of ozone gas (4.0 L·min^{-1}) produced from ordinary grade air passed through polycarbonate filters, and subsequently enriched with oxygen. The system consisted of an ozone generator (Model 6020, Rilize, Gijón, Spain), a flow controller Bronkhorst® (Model F-201AV, Ruurlo, The Netherlands), and an ozone on-line analyzer (Model 964C, BMT Messtechnik GMBH, Berlin, Germany). Ozone consumption was pH dependent, but did not resulted significantly different among the tested ions presence, resulting 0.39 ± 0.05 g/L when the initial pH value of the solution was not adjusted (pH=5.7); 0.48 ± 0.06 g/L when the pH was maintained at 6.5; and 0.67 ± 0.07 g/L for a constant pH = 12.0. Unconsumed ozone was sent to a catalytic ozone destructor.

A peristaltic pump (Masterflex® Console Drive, Cole-Parmer Instrument Company, Illinois, USA) was used to recirculate the solution under treatment (1 L) through the reactor, and probes for pH and redox potential and dissolved oxygen (ProODO, YSI Inc., Ohio, USA) measurement. Temperature was kept at 25ºC using a thermostatic bath (Model FL300, JULABO Labortechnik GmbH, Seelbach, Germany), which was aided by the reactor glass jacket itself.

Every experiment was performed for 30 min. The initial pH value of the prepared phenol solution (200 mg·L^{-1}) averaged 5.7 (±0.2), and was not modified by the addition of SO_4^{2-}, Cl^- or NO_3^-. During the first 5 min of ozone treatment, pH decreased to approximately 3.2, and was kept more or less constant thereafter. On the other hand, the addition of Na_2CO_3 caused pH to rise to about 12 to 13 (depending on the added concentration), and was kept buffered by the presence of HCO_3^-/CO_3^{2-} ions, as it was previously described when performing photocatalytic trials. When the initial pH was adjusted to 5.7 after the addition of Na_2CO_3, it resulted to rise to a 6.5 constant value after 5 min. In order to set proper comparisons, additional experiments were therefore carried out for every considered ion keeping the pH value constant at 6.5 and 12.0. 1M H_2SO_4 was added to acidify the solution in the experiments performed in the presence of HCO_3^-/CO_3^{2-}; whereas 1N NaOH was used for increasing and keeping constant the pH in the experiments developed at pH=6.5 and 12 when no ions or SO_4^{2-}, Cl^- and NO_3^- were added.

Analytical methods

On-line pH, redox potential, and dissolved oxygen measurements were carried out every minute. The degradation of phenol was assessed as the achieved reduction in chemical oxygen demand (COD), which was measured according to the Standard Methods for the Examination of Water and Wastewater (APHA, 2005) by the colorimetric method at 600 nm using an Aquamate-spectrophotometer (Thermos Scientific AQA 091801, Waltham, USA).

Statistical analysis

One-way ANOVA was run (Statplus, 2009) to determine the significance of the observed differences among experiments. *Post hoc* all pairwise comparisons were performed using Tukey's test ($P < 0.05$). Linear regression was used to explain the strong relationship between some treatment variables.

Results and discussion

UV/TiO$_2$ oxidation

The UV/TiO_2 oxidation treatment of phenol achieved a 23% reduction of the COD in the absence of inorganic anions, and the process was not significantly affected by the presence of Cl^-, SO_4^{2-} or HCO_3^-/CO_3^{2-} (Figure 1). In absolute terms, while the removal of COD decreased ≤ 3% when Cl^- or HCO_3^-/CO_3^{2-} were added at any of the tested concentrations, the presence of SO_4^{2-} increased the efficiency of the treatment an additional 2-3%. These non-significant effects were shown along the whole performance of the treatment (e.g. Cl^-, Figure 2A), indicating that SO_4^{2-}, Cl^-, and HCO_3^-/CO_3^{2-} were non-effective radical scavengers, nor competitors for active sites on TiO_2, in the performed photocatalytic degradation of phenol; whereas the oxidative contribution of $SO_4^{\cdot -}$ radical was confirmed (10, 21-24).

On the other hand, a significant increase in the reduction of the COD was observed when NO_3^- was added to the solution (Figure 1). While the addition of 250 mg·L^{-1} of NO_3^- enhanced the removal of COD up to a 31%, the presence of the highest tested dosage of 2000 mg·L^{-1} achieved an almost 37%. Differences among results produced at different NO_3^- concentration were not statistically significant; so the presence of 250 mg·L^{-1} of NO_3^- was enough to almost saturate the potential effect. In addition, almost all the improvement of the oxidation efficiency was produced during the first 15-30 minutes of treatment, as denoted by the observed changes in the slopes of the curves illustrating the evolution of the removal of COD along reaction time (Figure 2B). All the curves, whether in the presence or the absence of NO_3^-, keep more or less parallel thereafter; thus showing no further treatment enhancement.

A brown colour that progressively darkened the solution was observed along photocatalytic treatment in the presence of NO_3^-, suggesting the formation of some chromatic phenol derivatives (e.g. benzoquinone (39, 47, 48)); whereas no remarkable colour change was noticed in the presence of other anions. The presence of NO_3^- (or $NO_3\cdot$ radical) may therefore be able to drift phenol's route of degradation towards the production of certain intermediates that accumulate near TiO_2 particles and accelerate further intermediate coupling reactions on its surface (18, 49). In addition, some authors have proved the ability of NO_3^- to absorb UV-light yielding $OH\cdot$, which may represent a strong homogenous "accelerating" effect for the ongoing photo-degradative process (25, 50, 51).

When the solution was not acidified after the addition of Na_2CO_3, the produced buffered alkaline pH values (10-12) strongly reduced the removal of COD in comparison to the experiments performed at an initial pH=5.0 (COD removal ≈ 22.5%, Figure 3A), which results were identical to those achieved adjusting pH=4.0. As a higher concentration of CO_3^{2-} was added, a higher pH value was reached, and a lower removal of COD was achieved. In the presence of 250 $mg \cdot L^{-1}$ of CO_3^{2-} (pH≈10.5), the reduction of the COD dropped to ≈12%; whereas at the highest concentration of 2000 $mg \cdot L^{-1}$ (pH≈11.5), a poor 5% removal was just achieved after a 2-hours oxidation treatment.

This effect of the presence of CO_3^{2-} has been previously attributed to the production of $CO_3^{-}\cdot$ radical, which scavenges $OH\cdot$, and therefore causes poorer COD removal efficiencies (15, 26, 35-37). In order to check this out, further trials were performed in the absence of anions adjusting pH to 12.0 (± 0.2). Very poor results (COD removal < 5%), equal to those produced in the presence of a high amount of CO_3^{2-}, were achieved. A radical scavenging effect may therefore be neglected; whereas a strong effect of pH itself was supported (Figure 3B). As TiO_2 surface is negatively charged at pH>6.8, and the presence of phenol as negatively-charged phenolate species is significant at higher pH values, its adsorption on the surface of the catalyst is therefore hindered by the action of repulsive electrostatic forces (22, 27, 28). In addition, a lower degradation rate at higher pH values has been attributed to the fact that a higher concentration of OH^- prevents UV-light from penetrating the solution to effectively reach the surface of the catalyst (52).

Ozonation

In the absence of inorganic anions, the ozone oxidation of phenol produced a 55% removal of COD after a 30-minute-treatment without adjusting the pH (Figure 4A); whereas the addition of SO_4^{2-}, Cl^-, or NO_3^- resulted in a non-significant detrimental effect on the treatment efficiency (COD removal ≥50% in any case). A similar pH evolution along the treatment was observed in the absence of anions and when SO_4^{2-}, Cl^-, or NO_3^- were added to the solution; that is, initial pH averaged 5.7 ± 0.2, and then decreased to 3.2 ± 0.2 along the first 5 min of treatment, keeping more or less constant thereafter (the formation of carboxylic acids in the degradation process of phenol may acidify the solution, e.g. (53-56)). In addition, whether in the absence of anions or in the presence of SO_4^{2-}, Cl^-, or NO_3^- in the solution, no significant differences were shown in the reduction of COD along the whole treatment time, as shown for all tested SO_4^{2-} concentration values in Figure 4B. SO_4^{2-}, Cl^-, and NO_3^- were therefore ineffective radical scavengers when phenol was treated by ozone oxidation under acid conditions.

Provided there is a pH threshold below which the leading degradation mechanism of the ozonation treatment of every organic substance in the solution is direct oxidation by molecular ozone, and above which indirect oxidation after O_3 decomposition to $OH\cdot$ is predominant (11), and considering the above reported results under pretty strong acid conditions, it is reasonable to suppose that direct ozonation is widely dominating the oxidation process; thus potential radical scavengers could not produce much effect on the results.

On the other hand, the addition of CO_3^{2-} to the solution increased pH to basic values and the removal of COD was improved in comparison to when no anions were added and pH was not adjusted (Figure 5A). While the addition of 250 $mg \cdot L^{-1}$ of CO_3^{2-} (pH≈12.5-9.5) increased the efficiency of the 30-minute ozonation treatment close to a 60% COD removal, the addition of 500 $mg \cdot L^{-1}$ (pH≈13.0-10.5) significantly increased the efficiency of the treatment to about the 65%. No significant greater enhancement was achieved adding up to 2000 $mg \cdot L^{-1}$ of CO_3^{2-}.

When ozonation treatment was carried out in the absence of CO_3^{2-}, but pH was adjusted to similar basic values (pH≈12-11), the reduction of the COD resulted even higher (≈70%; Figure 5A); which supports the hypothesis that this apparent removal enhancement attributed to the presence of CO_3^{2-} was really caused by the increase of the pH value itself, which promotes the production of $OH\cdot$ radical when OH^- anion concentration is higher (33, 34). In fact, the ozonation process seems actually partially hampered after the addition of CO_3^{2-} when the results achieved at similar pH values are compared, which has been previously explained by an $OH\cdot$ scavenging effect (32, 34, 35). Finally, the effect of CO_3^{2-} on the ozonation efficiency of phenol was mainly produced during the first 10 minutes of treatment; after 20 minutes, no further effect was accounted for, as denoted by the changes in the slopes of the curves representing the evolution of COD removal along the time this treatment was performed (Figure 5B).

In order to compare further results under acid conditions, pH adjustment to 5.7 was set after the addition of Na_2CO_3. After several attempts, it was checked out that the actual pH value was buffered to 6.5 (±0.2) by the air present in the bubble column and the action of HCO_3^-/CO_3^{2-} equilibrium. The addition of 500 mg·L^{-1} of CO_3^{2-} under these conditions enhanced significantly the degradation of phenol by ozone, producing up to a 68% COD removal; whereas in the absence of ions, or when the addition of an equivalent concentration of the other tested anions, it resulted in about a 55% reduction of the COD if pH was not adjusted ($pH=5.7 \pm 0.2$; Figure 6). On the other hand, when all the experiments were repeated adjusting the pH to 6.5 or 12, it resulted that about the 75% of the initial COD was removed, whether no inorganic anion was added to the solution, whether SO_4^{2-}, Cl^-, or NO_3^- were added.

These results show that, regardless whether direct or indirect oxidation is the leading mechanism in the ozonation treatment of phenol, the presence of SO_4^{2-}, Cl^-, and NO_3^- is not significantly scavenging radicals and does not significantly affect the degradation process. It is additionally shown that ozonation treatment is significantly enhanced at a pH value close to neutral (6.5), or under basic conditions (12.0), which was surely caused by the promotion of OH· indirect oxidation (11). On the other hand, it has been also addressed that the ozonation rate of phenolic compounds increases at higher basic pH values, as it also does the degree of deprotonation and dissociation into phenolate species (57). The oxidation treatment efficiency is therefore also improved under these conditions because the ozone-phenolate reaction is faster than the ozone-phenol one (40). Finally, the significant lower COD removal rate addressed to the addition of CO_3^{2-} supports a radical scavenging effect that has been previously attributed to the presence of HCO_3^-/CO_3^{2-} (31, 32).

Conclusions

Although other authors have reported inconclusive to even contradictory conclusions regarding the effect of inorganic anions on the performance of several AOPs, it has been really demonstrated with statistical significance that the addition of SO_4^{2-} and Cl^- did not reduce the efficiency of the photocatalytic treatment of phenol when the pH of the solution was not adjusted ($pH \leq 5$); and an identical negligible effect was found when CO_3^{2-} was added and pH was adjusted to similar acid values.

On the other hand, the presence of NO_3^- significantly enhanced the photocatalytic reduction of the COD (≈15%). This effect may be explained by the ability of NO_3^- to absorb UV light, leading to an additional production of OH· radicals; the enhancement of the adsorption of phenol on the surface of TiO_2; and the acceleration of intermediate reactions on the catalyst surface.

The addition of CO_3^{2-} without pH adjustment resulted in an apparent loss of efficiency of the photocatalytic treatment of phenol, which was really caused by the generated higher pH value itself ($pH \approx 10.0\text{-}12.0$), as phenol adsorption on the catalyst surface was hampered under alkaline conditions due to the repulsive electrostatic forces that are manifested (both TiO_2 surface and phenolate species are negatively charged at such alkaline pH values).

Likewise, the presence of SO_4^{2-}, Cl^-, or NO_3^- did not reduce the efficiency of the treatment to a significant extent when phenol was oxidized by ozone; whether results without adjusting the initial pH value of the solution (pH=5.7) were always 15-20% worse in terms of the achieved reduction of the COD than those performed under adjusted close to neutral (pH=6.5) or basic (pH=12.0) conditions.

Finally, the addition of CO_3^{2-} negatively affected the efficiency of ozonating phenol by a 5-10% COD removal due to the manifested radical scavenging effect under both close to neutral (pH=6.5) and basic (pH=9.5-13.5) conditions; whereas there was no such an effect when the pH was adjusted to keep its initial acid value (pH=5.7).

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Figure captions

Figure 1. Reduction of the COD after a 2h photocatalytic oxidation treatment of phenol (200 mg·L^{-1}) in the absence and after the addition of chloride, sulphate, or nitrate without pH adjustment (initial pH=5.0±0.2); or in the presence of carbonate at pH=5.0 (Mean ± standard deviation, n=3-6. Letters label homogeneous groups of values).

Figure 2. COD removal evolution along the UV/TiO_2 oxidation treatment of phenol (200 mg·L^{-1}) without pH adjustment (initial pH=5.0±0.2) in the presence of **(A)** chloride, or **(B)** nitrate (Mean ± standard deviation, n=3-6).

Figure 3. (A) Reduction of the COD after a 2h photocatalytic oxidation treatment of phenol (200 mg·L^{-1}) in the presence of carbonate without adjusting the pH (Mean ± standard deviation, n=3-6. Letters label homogeneous groups of values). **(B)** A strong correlation was found between pH and COD removal when UV/TiO_2 treatment was performed under alkaline conditions in the presence or the absence of carbonate.

Figure 4. (A) Removal of COD after a 30-min ozone oxidation treatment of phenol (200 mg·L^{-1}) in the absence of inorganic anions and in the presence of chloride, sulphate and nitrate without adjusting the pH (initial pH=5.7±0.2). (Mean ± standard deviation, n=3-6. n.s.=non-significant differences were found). **(B)** The evolution in time of the reduction of the COD in the presence of sulphate is shown as an example.

Figure 5. (A) Reduction of the COD after a 30-min ozone oxidation treatment of phenol (200 mg·L^{-1}) in the absence of anions at pH=5.7 or 12; and after the addition of carbonate without adjusting the pH (Mean ± standard deviation, n=3-6. Letters label homogeneous groups of values). **(B)** Evolution in time of the removal of COD in the absence of anions at pH=12, and in the presence of carbonate without pH adjustment.

Figure 6. COD removal after a 30-min ozonation treatment of phenol (200 mg·L^{-1}) in the absence or the presence (2000 mg·L^{-1}) of sulphate, chloride, nitrate, or carbonate with or without adjusting the pH.

FIGURE 1

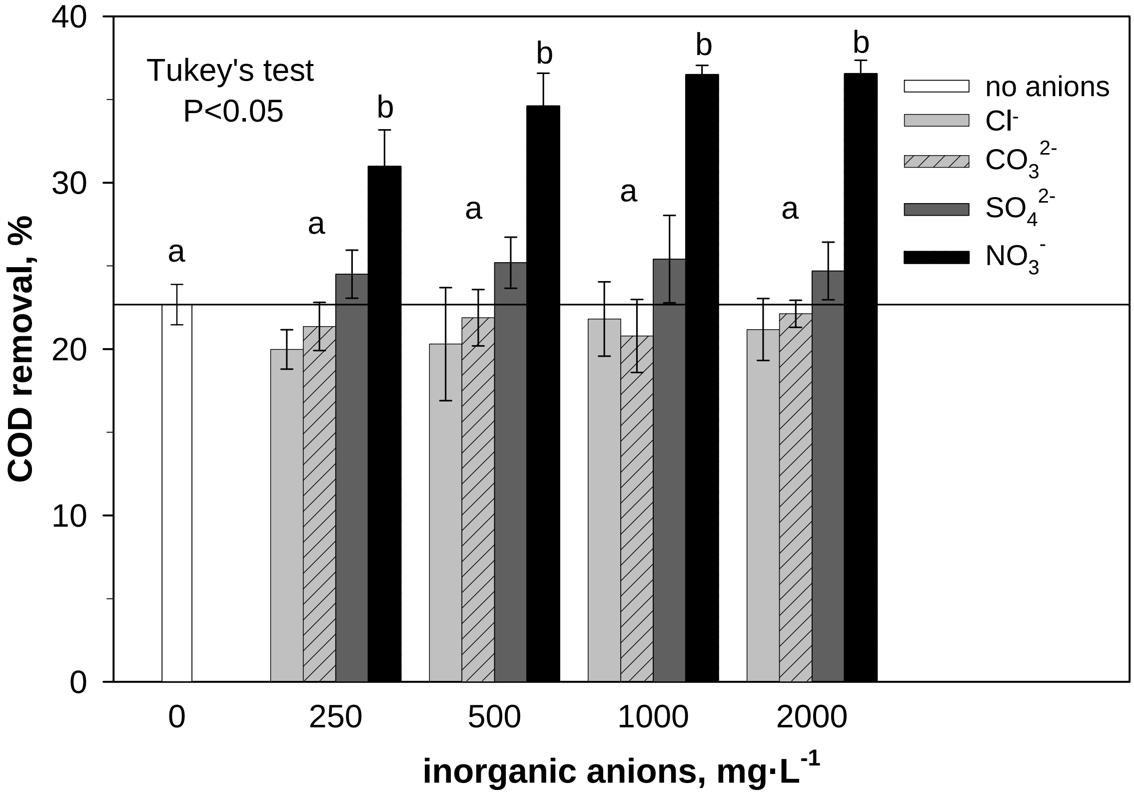
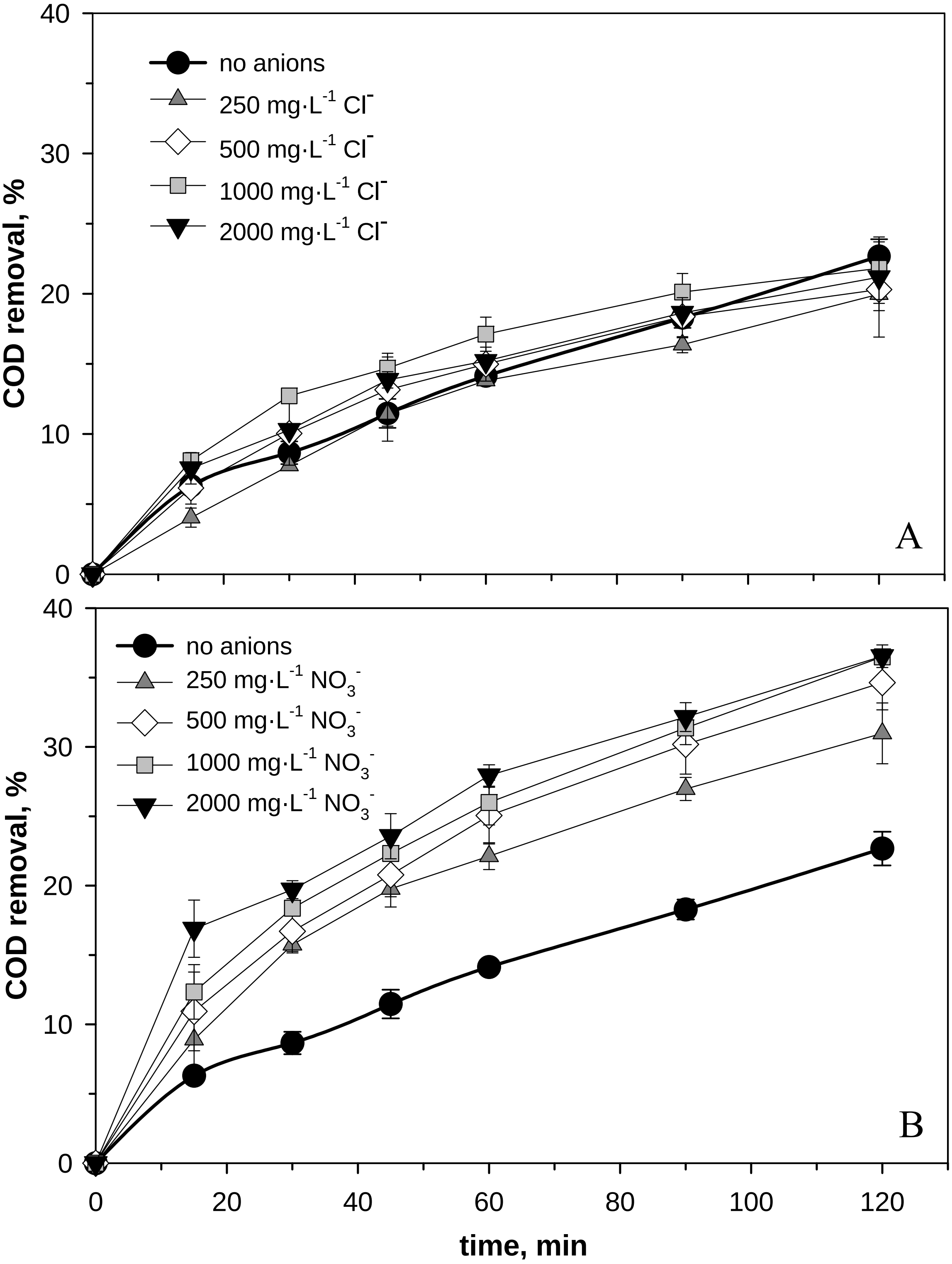

Tukey's test
P<0.05
no anions
Cl-
CO3 2-
SO4 2-
NO3 -
a
a
b
a
b
a
b
a
b
40
30
20
10
0
COD removal, %
0
250
500
1000
2000
inorganic anions, mg·L-1

FIGURE 2



40
30
20
10
0
COD removal, %
no anions
250 mg·L^{-1} Cl^{-}
500 mg·L^{-1} Cl^{-}
1000 mg·L^{-1} Cl^{-}
2000 mg·L^{-1} Cl^{-}
A
40
30
20
10
0
COD removal, %
no anions
250 mg·L^{-1} NO$_3^{-}$
500 mg·L^{-1} NO$_3^{-}$
1000 mg·L^{-1} NO$_3^{-}$
2000 mg·L^{-1} NO$_3^{-}$
B
0
20
40
60
80
100
120
time, min

FIGURE 3

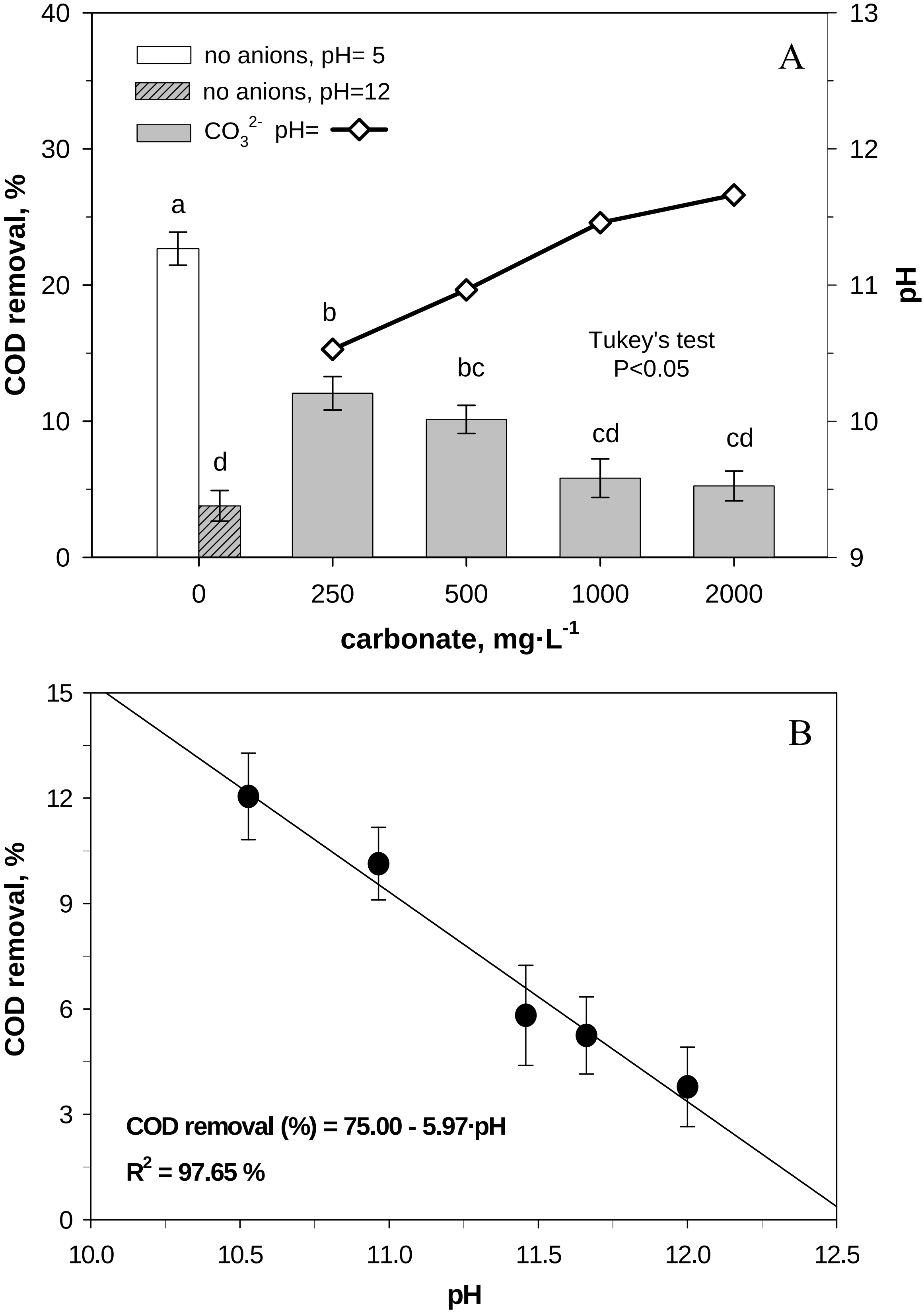

A
no anions, pH= 5
no anions, pH=12
CO3 2- pH=
a
b
bc
cd
cd
d
Tukey's test
P<0.05
COD removal, %
pH
0
10
20
30
40
9
10
11
12
13
0
250
500
1000
2000
carbonate, mg·L-1
B
COD removal (%) = 75.00 - 5.97·pH
R2 = 97.65 %
COD removal, %
0
3
6
9
12
15
10.0
10.5
11.0
11.5
12.0
12.5
pH

FIGURE 4

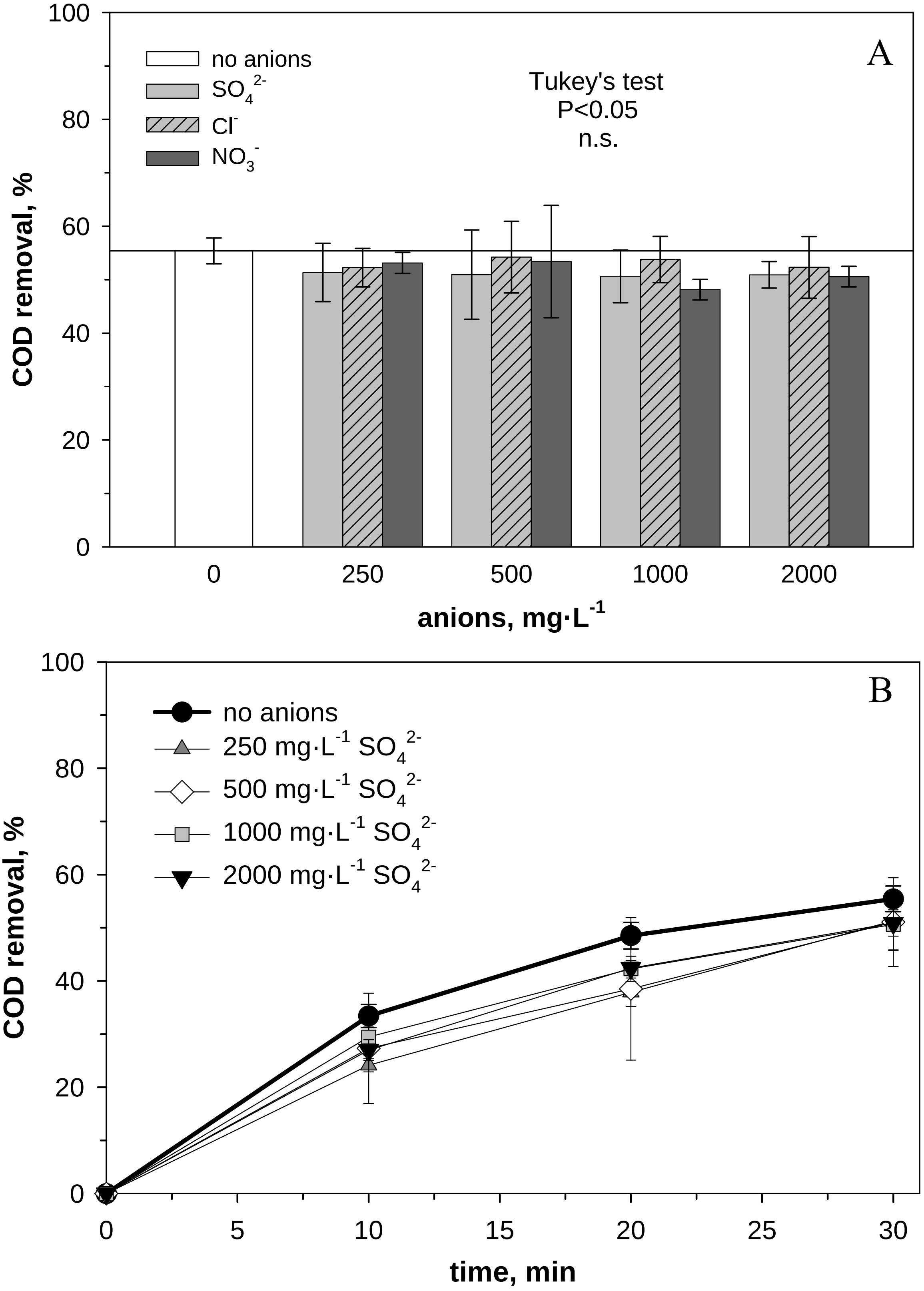
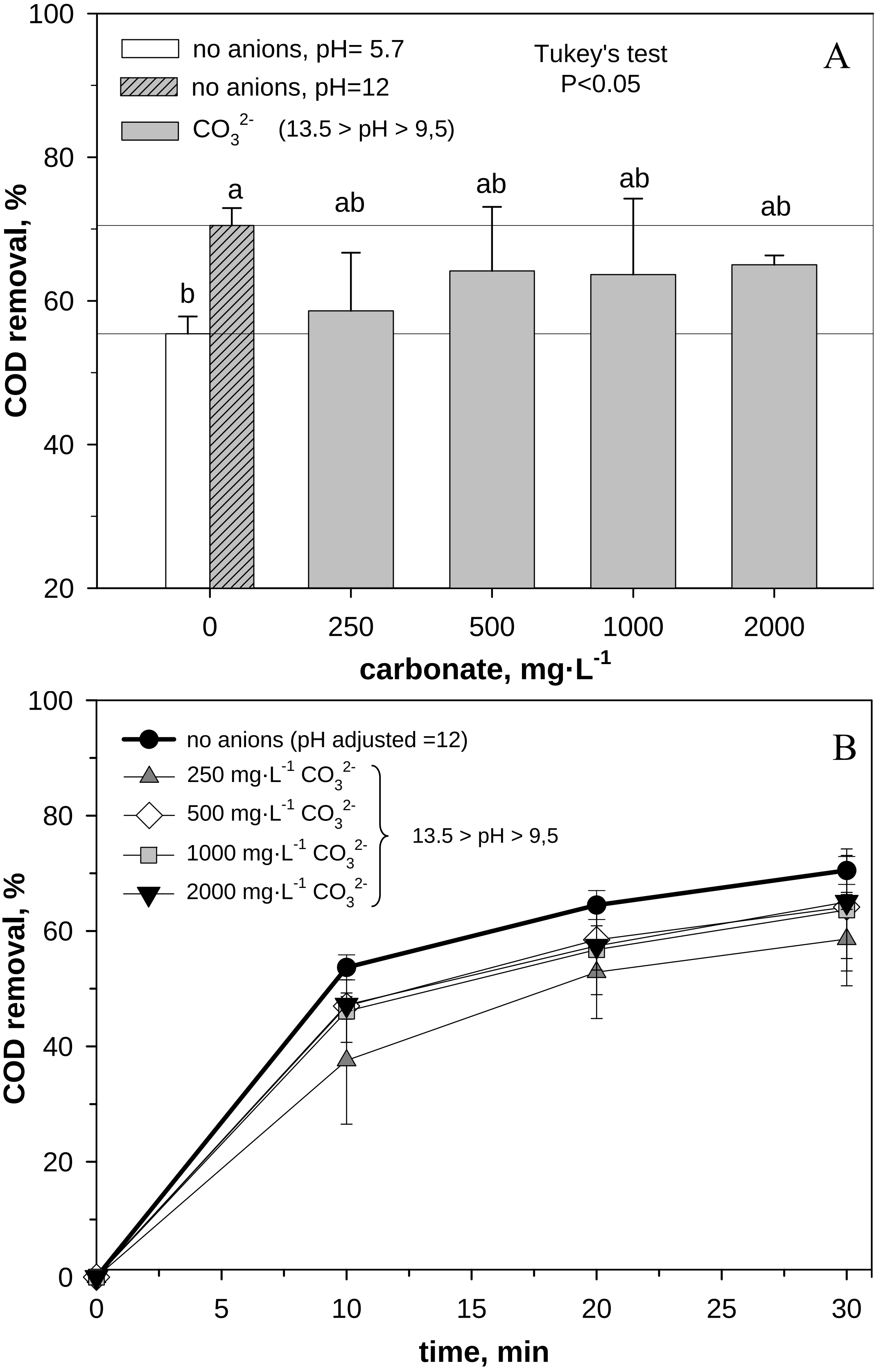
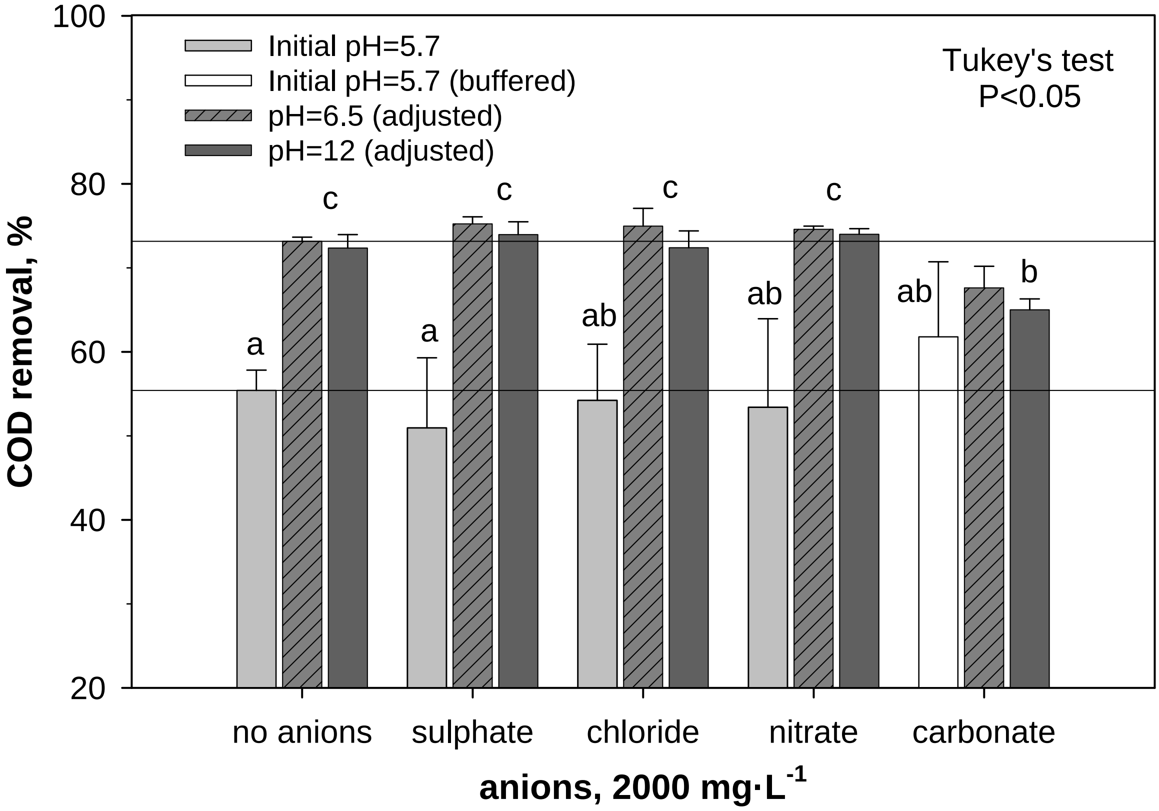

A
no anions
SO$_4^{2-}$
Cl$^-$
NO$_3^-$
Tukey's test
P<0.05
n.s.
COD removal, %
0
20
40
60
80
100
0
250
500
1000
2000
anions, mg·L^{-1}
B
no anions
250 mg·L^{-1} SO$_4^{2-}$
500 mg·L^{-1} SO$_4^{2-}$
1000 mg·L^{-1} SO$_4^{2-}$
2000 mg·L^{-1} SO$_4^{2-}$
COD removal, %
0
20
40
60
80
100
0
5
10
15
20
25
30
time, min

FIGURE 5



100
80
60
40
20
COD removal, %
no anions, pH= 5.7
no anions, pH=12
CO_3^{2-} (13.5 > pH > 9,5)
Tukey's test
P<0.05
A
b
a
ab
ab
ab
ab
0
250
500
1000
2000
carbonate, mg·L^{-1}
100
80
60
40
20
0
COD removal, %
no anions (pH adjusted =12)
250 mg·L^{-1} CO_3^{2-}
500 mg·L^{-1} CO_3^{2-}
1000 mg·L^{-1} CO_3^{2-}
2000 mg·L^{-1} CO_3^{2-}
13.5 > pH > 9,5
B
0
5
10
15
20
25
30
time, min

FIGURE 6


100
80
60
40
20
Initial pH=5.7
Initial pH=5.7 (buffered)
pH=6.5 (adjusted)
pH=12 (adjusted)
Tukey's test
P<0.05
a
c
a
c
ab
c
ab
c
ab
b
COD removal, %
no anions
sulphate
chloride
nitrate
carbonate
anions, 2000 mg·L-1