

Review

Photoactive Materials for Decomposition of Organic Matter Prior to Water Analysis—A Review Containing Original Research

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Abstract: Water plays a fundamental role in meeting the basic needs of society. Surface waters contain numerous organic pollutants, such as pesticides, drugs, and surfactants. The use of photolysis processes in organic matter degradation not only has practical applications in wastewater treatment but is also of major importance in the pretreatment of samples prior to the trace analysis of numerous analytes. The heterogeneous degradation is simple to implement prior to ultra-traces determination and is the only one allowed before the speciation analysis. Speciation analysis is currently the most important environmental challenge. The analysis of water, including tests associated with wastewater pretreatment and the monitoring of aqueous ecosystems, is the largest segment of environmental analysis. In the trace analysis of water, organic compounds are the principal interfering compounds reducing the quality of the obtained results or even preventing the determination of the examined analytes altogether. Some analytical techniques do not perform well in the presence, for example, of surfactants, so mineralization is sometimes required. Advanced oxidation processes are used to remove interfering organic compounds. The oxidation can be performed using homogenous photolysis (UV mineralization with hydrogen peroxide addition), while heterogenous photolysis using semiconductors helps to increase the removal efficiency of interferents dissolved in water. Utilizing semiconductor nanostructured materials as photocatalysts has been shown to be effective for the adequate removal of a wide spectrum of pollutants in water. Several semiconductor systems are used in the degradation of organic compounds, e.g., TiO_2 , Fe_3O_4 , WO_3 , Fe_2O_3 , ZnO , and mixtures of these oxides enriched with various precious metals, such as silver or gold. It is very challenging to manage the selectivity and reduction power so that organic compounds can be degraded but without disturbing the speciation of As, Cr, or Tl. Chemical modification of samples and the selection of semiconductor layers, light wavelength, and pH allow for the targeted degradation of specific compounds but may also indirectly affect the analysis of water samples. This review is a presentation of the state of the art of photocatalysis as a simple and effective technique for sample pretreatment in ultra-trace and speciation analysis and its critical as well as unpublished data related to this topic.

Keywords: photodegradation of organic matter; photoactive materials; environmental remediation; trace analysis; speciation analysis; wastewater; speciation arsenic; speciation thallium; speciation chromium



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1. Aspects of the Use of Photolysis in Water Analysis

Water can be a complex chemical system, often comprising multiple phases; it can hold substances in solution or suspension. It is essential for meeting the basic needs of society and is a natural habitat for many species of plants and animals while also significantly influencing geochemical and physicochemical processes [1–3]. Surface waters contain numerous organic pollutants, such as pesticides, drugs, and surfactants, occurring in the form of solutions and suspensions [4,5]. Suspended particulate matter (SPM), containing particles above $0.45\ \mu\text{m}$ [3,6], consists mainly of inorganic colloids in the form of oxides, carbonates, dioxides, organic matter, and microorganisms. This phase is an important constituent of natural waters due to the possibility of transporting chemical

species adsorbed on it [7]. The adsorption depends on various properties of the suspension, such as the composition, shape, and size of the suspended particles. Adsorption on suspended particles affects the bioavailability of substances present in water and reduces their content in the dissolved phase. Under the influence of the ongoing natural chemical and biochemical processes, their desorption is also possible [5,8].

The use of photolysis for the degradation of organic matter has a practical application in wastewater treatment, but it is usually the final element of processing after rapid filtration and biological treatment [9,10]. The combination of UV decomposition with ozone treatment has practical applicability. The principal mechanism of this combination is the generation of highly reactive free radicals: at a larger scale, the combination enhances free radical generation, which eventually leads to higher oxidation rates [11]. The use of oxidation with UV radiation in the presence of titanium dioxide has often been studied, publications describing both the technical principles and attempts to implement this technology. This technique tends to be used for either air purification or sterilization. However, the application of heterogeneous degradation based on photocatalysis in wastewater treatment or water treatment at public waterworks is still in the future [12,13]. Photolysis in heterogeneous systems, as an advanced oxidation technique, attracts the attention of researchers because it involves the direct use of solar energy in removing pollutants introduced into the natural environment. The mechanism of the phenomenon was well described in some previous articles [13]. Environmental remediation has not been implemented as it is associated with low efficiency in polluted waters and high costs [14]. This type of degradation system works well as an analytical technique for simplifying the matrix, e.g., the degradation of organic compounds prior to the analysis of polluted water.

The analysis of water, including tests involved in wastewater pretreatment and the monitoring of water ecosystems, is the largest segment of environmental analysis. Organic compounds can reduce the environmental quality of water or its suitability for consumption [14]. Even in cases when the organic matter content naturally increases, the water fraction may need to be degraded for practical and hygienic reasons. The removal can be performed using anionic exchange resin [15], ozone treatment [16] with UV and/or chemical supports [17–20], or photocatalysis [21].

Another important problem is contamination with pharmaceuticals, which show significant resistance and are not completely removed from wastewater by conventional treatment methods [22]. Advanced oxidation processes, involving reactive oxygen species (principally hydroxyl radicals), are used to remove more resistant polluting substances. The oxidation can be performed using homogeneous photolysis [23], but using heterogeneous photolysis with semiconductors helps to increase the efficiency of the destruction of pharmaceuticals dissolved in water [24]. For this type of decomposition, titanium oxide and UV light, as well as tungsten trioxide and visible light, can be used. The decomposition (80–100%) of naproxen, paracetamol, diclofenac, and ibuprofen was obtained using TiO_2 and UV light [25,26]. Visible light is also used for photo-biostability (decomposition of pathogens) of water but using a variety of semiconductors [27]. Tungsten and iron oxides are semiconductors that give rise to photochemical activity in the spectral range of sunlight. For some antibiotics, i.e., tetracyclines, the obtained degradation using WO_3 ranged from above 60% up to 80% [28,29]. In the case of Fe_2O_3 , the efficiency of the decomposition was only 30–50% [30].

In samples of relatively pure water, both surface and underground, there may be suspensions in which there are large quantities of so-called organics. However, even in such situations, the analysis of trace elements requires some method for the simplification of organic matter [21]. Surfactants are ubiquitous substances where human activity affects aquatic ecosystems. These substances strongly interfere with many techniques for the analytical study of xenobiotics. Digestion is, therefore, required, wet closed mineralization accelerated with microwave energy mostly being applied, especially when the water contains high concentrations of surfactants [3]. In the case of water samples, semiconductor-supported digestion is as effective as wet digestion. The former method is environmentally

friendly and ensures complete mineralization. Mineralization with the use of UV or visible radiation does not require using such large amounts of reagents, which decrease the limit of detection [5,31–34]. There are many aspects to using photocatalysis for the analysis/monitoring of aquatic ecosystems. It is a tool that can successfully modernize and improve such tests.

2. Photoactive Materials for Decomposition

Utilizing nanostructured semiconducting materials as photocatalysts has been shown to be effective for the adequate removal of a wide spectrum of pollutants in water and air treatment. Most photocatalytic materials are, however, wide-bandgap semiconductors and are, therefore, active only under UV irradiation. Nanostructured materials reveal exclusive properties, such as photocatalytic activity, high mechanical strength, thermal stability, electrical conductivity, and a high surface-area-to-volume ratio. This latter feature of nanomaterials has contributed to the higher adsorption of various types of pollutants, enabling their effective photocatalytic degradation.

Among the many currently used semiconductors, titanium oxide, or, rather, its various modifications, remains one of the important materials in environmental remediation applications because of its high oxidation efficiency, nontoxicity, high photostability over a broad pH range, chemical inertness, and eco-friendly properties. Moreover, the cost of TiO_2 is low owing to the relatively high natural abundance of Ti in Earth's crust. The redox potentials of its conducting band (CB) and valence band (VB) simultaneously cover the reduction of O_2 and the oxidation of water. On the other hand, TiO_2 , in common with many other semiconductor photocatalysts (e.g., ZnO), has a broad energy gap, so only 4–5% of the total solar radiation is effectively utilized. Thus, solar irradiation cannot be applied to move the electron up to the CB, and additional UV sources are needed, making this process energetically unfavorable. Therefore, research on the scope of TiO_2 has been mostly focused on the development of preparation methods to increase wavelength absorption in the visible light spectrum and to hinder electron–hole recombination by doping or modifying its surface.

Currently, four types of pollutants can be highlighted with respect to photodegradation studies: dyes, pharmaceuticals, surfactants, and volatile organic compounds. There have been various studies comparing TiO_2 -based photocatalytic materials in pristine and hybrid systems. One strategy is the doping of TiO_2 with transition metals (e.g., iron, nickel, vanadium, chromium, gold, or silver), leading to the formation of new energy levels between the VB and CB, allowing the absorption of visible light as well as acting as electron traps preventing electron–hole recombination [35,36]. For example, Chen et al. [37] showed the highly oxidative behavior of a silver-modified TiO_2 photocatalyst for degrading organic dyes and derivatives of benzothiophene under visible light irradiation, which could be related to the plasmonic effect of Ag nanoparticles. In addition, Tseng et al. [38] examined carbon-modified Ag/ TiO_2 nanocomposites produced using a co-impregnation method for the removal of nitrogen oxides under both visible light and UV irradiation. The observed enhancement of the photocatalytic removal of nitrogen oxides by such photocatalytic materials under visible light irradiation could be related to the synergistic effect of the carbon and silver species. In our research, we proposed the use of a TiO_2 layer as an oxidation medium for the photodegradation of the organic matrix during the determination of cadmium and lead in wastewater samples with a high amount of organic matter [33]. The results indicated that the recovery of lead was in the range of 99–103% for digestion with anatase immobilized in quartz tubes, which indirectly proved that the decomposition of organic matter was complete. The lead determination using voltammetry is extremely sensitive for the existence of organic compounds, even at a trace level [20]. The obtained results of Cd or Pb determinations in the presence of even traces of organic compounds are significantly underestimated.

Titanium dioxide photocatalysts doped by non-metals, e.g., C, N, S, or P [39–42], metals, e.g., Cu, Ni, W, V [43–45], as well as noble metals, such as Pt, Ru, and Pd [46,47],

have also been used for the photodegradation of various compounds. For example, the presence of doped N atoms led to the formation of a new VB (mid-bandgap orbital) with a shifted VB edge that narrowed the bandgap of TiO₂. Junwei et al. [48] examined N/F co-doped TiO₂ nanotube arrays produced using a sequence of solvothermal doping and annealing treatment of the photocatalytic materials. The obtained photocatalyst exhibited visible light absorption and low electron–hole recombination. Moreover, the N/F doping enhanced azo dye degradation and metal ion removal.

As well as organic pollutants, toxic inorganics can also be removed by using TiO₂ photocatalysts. Challagulla et al. [49] showed that TiO₂ deposited on the magnetic support Fe₃O₄ demonstrated superior activity compared to pristine TiO₂ toward Cr(VI) photoreduction in an aerobic atmosphere. A catalyst containing 30% TiO₂ exhibited the best photocatalytic activity for Cr(VI) photoreduction rate among those examined, as well as having good recoverability and recyclability. Another author [50] used the same semiconductor configuration, i.e., TiO₂ with Fe₃O₄, but additionally deposited it on graphene structures and applied it toward the photocatalytical removal of U(VI) from aqueous solutions. It was found that UV irradiation led to the enhancement of the photoreactivity of TiO₂/Fe₃O₄ for the reduction of U(VI) compared to using pristine TiO₂. In the context of Cr(VI) removal from environmental samples, it is worth noting a study on the use of TiO₂-modified graphitic carbon (GC) composites synthesized using *Staphylococcus aureus* as the biotemplate to modify commercial TiO₂ powder [51]. These TiO₂@GC composites, especially when heat-treated at 800 °C, possessed abundant hierarchical mesoporous structures and showed high catalytic activities toward Cr(VI) photoreduction under sunlight.

Recently, much interest has been directed toward the use of metal–organic frameworks in the synthesis of new photocatalysts. For instance, Rashid et al. [52] prepared a composite system based on Ni/Fe in MIL-101 and Na₂S precursors by heat treatment. The obtained NiS/ γ -Fe₂O₃/C type-II heterojunction system demonstrated a superior activity toward the photoreduction of Cr(VI), with an efficiency of 83.85% after 35 min illumination.

Another approach [53] utilized the conducting polymer polypyrrole (PPy) to modify a ZnTi hydrotalcite (ZnTi-LDH) by an in situ oxidation polymerization. It was found that the composite exhibited better photocatalytic performance for the reduction of Cr(VI) (efficiency of 99.72% for 35 min irradiation under visible light) than that of the single components of the composite. The authors assigned this behavior to the beneficial combination of the ZnTi-LDH stratified structure and conductive PPy, whereas, to obtain a new photocatalytic material demonstrating a high level of photoreduction of Cr(VI) of 99.02 %, PPy and an NH₂-MIL-125 metal–organic framework were employed [54]. Both examples demonstrate that the presence of conducting polymer (PPy) leads to an improvement in the separation and transfer of charge carriers in the composite system. An interesting concept of a photocatalytic system for the photoreduction of Cr(VI) based on a heterojunction has been proposed [55]. The Z-scheme Bi₂S₃-In₂S₃ photocatalyst was synthesized using a one-step hydrothermal method, achieving an enhancement of Cr(VI) photoreduction efficiency of practically 100% with excellent stability.

Apart from TiO₂, research on other semiconducting metal oxides, such as WO₃, Fe₂O₃, ZnO, MoO₃, ZrO₂, or composite systems containing two or three different semiconductors, and their utilization for remediation processes, has become increasingly important. One example of such photocatalysts is tungsten(VI) oxide, which is a promising semiconductor photoactive to visible light [56]. A bifunctional photocatalyst, a combination of hexagonal tungsten trioxide with reduced graphene oxide, has been used for the photodegradation of model organic pollutants, such as methyl orange, methylene blue, and rhodamine B [57]. The proposed photocatalytic system containing 1 wt.% of reduced graphene oxide provided a superior total removal efficiency of the abovementioned pollutants in comparison to its separate components. In our study, we demonstrated that a tungsten trioxide layer can be used successfully for the decomposition of dissolved organic matter containing the anionic surfactant sodium dodecyl sulfate (SDS) and the nonionic surfactant (1,1,3,3-tetramethylbutyl)phenyl-polyethyleneglycol (TritonTMX-114, Sigma-Aldrich, Milan, Italy)

in natural water samples prior to the determination of trace residues of lead by stripping voltammetry methods [5]. The results of the study showed that it was also possible to obtain a high efficiency of decomposition, equal in efficiency to that of the reference method, which was hydrogen peroxide oxidation assisted by UV, with evaporation nearly to dryness.

Another material [58] based on tungsten trioxide with reduced graphene oxide (rGO) and molybdenum disulfide (MoS_2) was utilized for the photodegradation of rhodamine B. This system, which contained a 10 % wt. fraction of MoS_2 -rGO, displayed a degradation rate of 98.3 % after 20 min visible light illumination. The enhancement in photocatalytic activity of the obtained material was explained by the authors based on Z-scheme system theory. Lately, a heterojunction based on polymeric graphitic carbon nitride combined with tungsten trioxide has achieved much attention because of its high chemical stability and the use of photocatalytic g- C_3N_4 . Such a heterostructure led to the enhancement of the electric field between both semiconductors, promoting the separation of photogenerated electrons and holes to the CB and VB, respectively. This heterojunction was utilized to enhance the photodegradation of tetracycline hydrochloride [59].

In order to enhance the photocatalytic efficiency of metal oxides (e.g., WO_3), the creation of hybrid materials is a practical approach that can be implemented by introducing additional semiconductors. In this area, a binary photocatalyst combining tungsten oxide with iron oxide (Fe_2O_3) nanoparticles deposited on graphene sheets [60] was fabricated via a hydrothermal method. The resultant hybrid system displayed enhanced photocatalytic removal efficiency for organic pollutants, such as rhodamine B or methylene blue, of more than 95% under sunlight illumination. Several reports have demonstrated the utilization of hierarchical photoactive films containing tungsten(VI) oxide and iron(III) oxide (hematite), prepared by a layer-by-layer method, for the decomposition of organic matter in the speciation analysis of arsenic, thallium, and lead in water samples [61,62]. The use of this hierarchical photocatalyst as an active film during visible light irradiation of a water sample resulted in the simplification of the organic matter and provided no speciation change in the abovementioned elements.

3. Photolysis in the Organic Matter Degradation Step Prior to Analysis

The results obtained with a precise and accurate measurement technique do not mean much when the analytical signals are interfered with by the presence of organic compounds. However, in the case of ultra-trace analysis or determination of individual forms of an element (speciation analysis), traditional mineralization (oxidation of organic compounds) is not an option [62,63]. The scheme of the analytical procedure of water samples is exhibited in Figure 1.

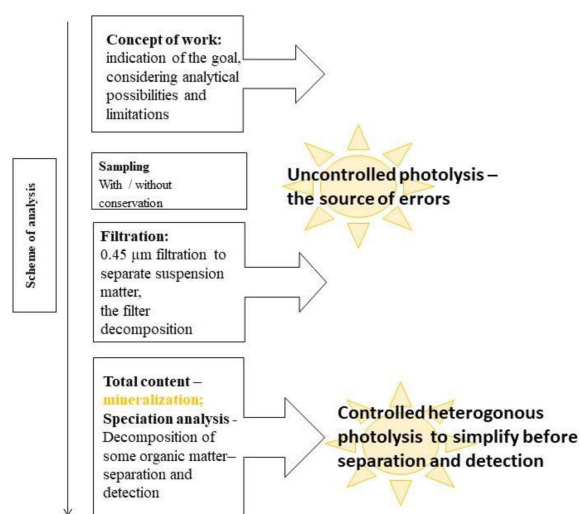


Figure 1. Scheme of ultra-trace speciation analysis of water in the context of photocatalysis.

3.1. Application in Trace Analysis

As a result of UV radiation, primary and secondary processes take place. Primary processes are caused directly by the absorption of UV radiation. When a molecule absorbs a photon, it becomes excited, which results in a chemical reaction. As a result, chemical bonds are broken, while organic compounds are transformed into other ones or completely decompose. Direct degradation by UV radiation only occurs when the incident light is absorbed by the substance. Secondary processes consist of the decomposition of organic matter as a result of the action of reactive species, such as ozone or singlet oxygen, formed after the absorption of the UV radiation quantum [14,18]. Some applications of UV degradation of organic matter before the determination of Zn, Cd, Pb, and Cu using anodic stripping voltammetry were reported [19,64]. However, UV mineralization sometimes does not obtain satisfactory results [33]. In order to increase its effectiveness, substances are added to the sample that support the decomposition of organic matter, including hydrogen peroxide, ozone, nitric (V) acid, and potassium persulfate. Only hydrogen peroxide is of practical use in photolysis [18], and, in the case of photocatalysis [21,31,64,65], WO_3 , Fe_2O_3 , ZnO , or TiO_2 are used in practice [34,66–70].

Digestion based on photodegradation is a technique supporting the analysis of water and can be a stage after wet mineralization when it is planned to use a technique that is particularly sensitive to the presence of organic compounds. Spectrometric techniques are more resistant toward the presence of organic substances in analyzed water samples, but, in the case of high surfactant contents, the nebulization step in the inductively coupled plasma system does not function properly. During analysis of a series of ions in the wastewater from a waste deposit heap after the flotation concentration of sulfide ores using inductively coupled plasma mass spectrometry (ICP-MS), it was found that, in the case of samples not subjected to earlier mineralization, approximately 28% of the total metal content was underestimated for all analytes [3].

Electrochemical techniques are particularly sensitive; they can even be used as sensors for the completeness of the organic matrix decomposition in water [71]. Stripping voltammetry was used to determine the concentrations of cadmium, zinc, lead, and copper in seawater samples taken from different depths. To mineralize the organic compounds, 12 h irradiation with UV radiation from a 500 W mercury lamp was employed. As a decomposition aid, a small amount of perhydrol (9 μL H_2O_2 / 10 mL of sample) was added so that it did not interfere with signal recording [72]. A self-constructed UV flow mineralizer was used for the removal of organic compounds from surface water samples, which contained a large content of surfactants, collected in the vicinity of a zinc ore mine [31]. For some voltammetric and atomic spectrometry determinations, trace amounts of hydrogen peroxide may perturb the measurements [33,64]. In addition, this technique for the preparation of samples increases the blank value, and, therefore, the application of heterogeneous photolysis is a superior technique.

A study of the optimization of TiO_2 -assisted photo-oxidation of wastewater prior to voltammetric determination (ASV, SWV) indicated that using only UV, with or without H_2O_2 addition, did not lead to consistent results with respect to determinations by ICP-MS (reference method); however, the application of TiO_2 and UV (1–2 h) assisted the decomposition of non-filtered wastewater samples, providing results statistically equal to those from ICP-MS. In addition, the procedure was characterized by higher sensitivity [33]. The use of titanium oxide and UV radiation requires the use of quartz vessels. The application of tungsten oxide makes it possible to reduce the cost of the analysis since there is no need to use quartz. A recovery study of Pb was carried out using anodic stripping voltammetry, with a hanging mercury drop electrode (HMDE, working electrode) being utilized as a sensor for the completeness of the surfactants' decomposition (SDS or TritonTMX-114). An HMDE was used because the mercury metal is sensitive even toward traces of surfactants, and the electrochemical signal suppression is very strong. Photo-mineralization using a solar lamp (1.5 AM, 380–800 nm) together with WO_3 was used as an alternative procedure

to digestion with hydrogen peroxide. Using a layer of photoactive semiconductors active in the wavelength range of sunlight allowed simple glass to be used for reaction vessels [5,33].

A very interesting technique is the employment of semiconductor layers organized and selected to meet the needs of analysts. The determination of traces of metals using stripping voltammetry was supported by the degradation of surfactants utilizing hierarchical and bicomponent admixtures of tungsten(VI) oxide and iron(III) oxide (hematite) [73]. The decomposition, or, rather, simplification, of SDS and Triton™X-114 reached 100% after 2 or 3 h, respectively, of solar-light-irradiation-assisted digestion in the case of mixed WO₃ and Fe₂O₃, as well as in a hierarchical system with an Fe₂O₃ layer between WO₃ layers. It should be emphasized that, depending on the layer system, it is possible to work with an acidified water sample (pH < 2—permanently to determine the total content) or an unmodified sample (4 < pH < 6—for speciation analysis). In Figure 2, the range of the % Pb recovery is shown, which was fully as expected following the effective heterogeneous photodegradation of a very resistant surfactant (Triton). Increasing exposure time caused not only a better recovery but, also, the precision of voltametric determination was expressed in % of the value spread, meaning that the decomposition was much better.

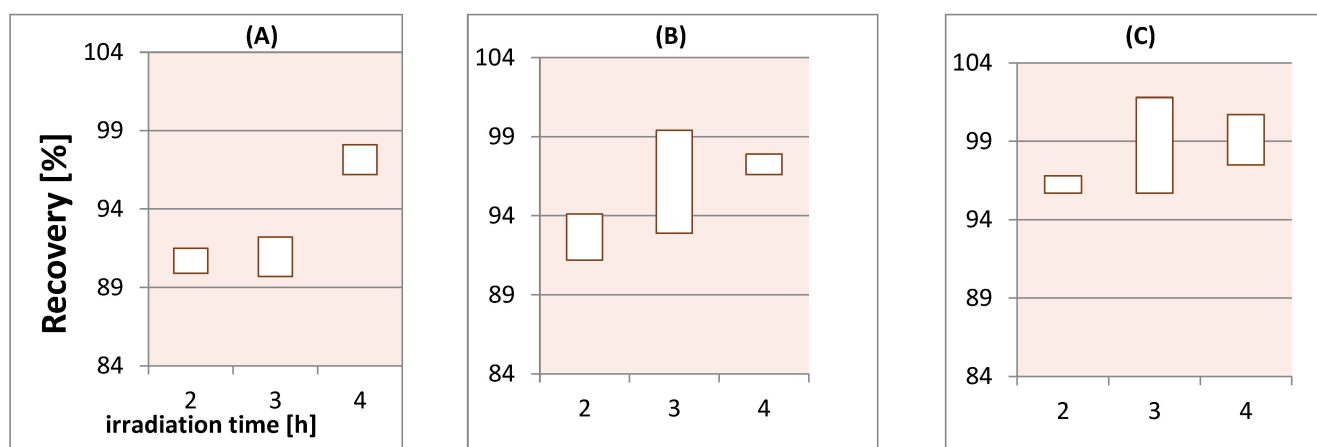


Figure 2. Comparison of the recoveries (in %) of the addition of 20 ng Pb in 23 mL solution of Triton solution with a concentration of $1.97 \times 10^{-5} \text{ mol L}^{-1}$ from the irradiation time of 23 mL for the active layer with a structure: (A) Fe₂O₃/WO₃/Fe₂O₃ (pH = 5), (B) WO₃/Fe₂O₃/WO₃ (pH = 2), (C) Fe₂O₃WO₃/Fe₂O₃WO₃/Fe₂O₃WO₃ (pH = 2) (unpublished scheme).

3.2. Application in Speciation Analysis

The toxicity, mobility, and bioavailability of some trace elements are highly related to their chemical species, and, therefore, modern environmental analysis includes speciation analysis. Usually, the separation of chemical forms of nutrients or xenobiotic substances is performed using chromatography with spectrometric detection, electrochemical analysis (stripping voltammetry), or specific techniques, i.e., cold vapor or hydrogen generation atomic absorption/atomic fluorescence/emission spectrometry. Most of these techniques require sample modification, and heterogeneous photocatalysis is quite a useful tool for such challenging research purposes.

It is necessary to include mercury speciation in environmental speciation analysis, especially in aquatic ecosystems. The chemical forms in water samples strongly depend on the redox conditions, with mostly Hg(II) complexes, methyl mercury, and dimethyl mercury being detected, along with metallic mercury [74–76]. The most dangerous mercury compounds are the organic forms, so distinguishing between chemical forms is important. A popular analytical technique is cold vapor generation with atomic absorption spectrometry [77], which is based on the reduction (SnCl₂) of the ionic form to the metallic form. The omission of the addition of this reducer and the use of photocatalysis is an interesting direction in developing this analytical procedure for the study of mercury speciation. A

photocatalytic method using UV light (253.7 nm) irradiation on the surface of a nano-TiO₂ layer on a glass fiber in the presence of a formic acid and sodium formate mixture as a hole scavenger has been used as an alternative to the reduction of Hg(II) using Sn(II) ions [74]. High potential can be used in this reaction (Ag-TiO₂ [78] or Au-TiO₂ [78]).

Selenium occurs in four typical species: Se(IV), Se(VI), selenocystine ((SeCys)₂), and selenomethionine (SeMet). Selenium is an element whose deficiency and excess can both cause harm, and its bioavailability is strong and depends on the form in which it occurs [79]. The method that is most applied for speciation analysis is hydride generation atomic absorption spectroscopy, the strong points of which are high selectivity and a low limit of detection [80]. An alternative to traditional chemical reduction could be photocatalytic vapor generation assisted by active layers of Ag-TiO₂ or ZrO₂. This system, in which the CB electron served as a “reductant”, was successfully applied to reduce selenium species, converting them directly into volatile H₂Se and reducing even Se(VI), the most reduction-resistant form of selenium [81].

Arsenic and thallium ions in the environment occur in various states of oxidation and form distinct species, which implies differences in their physicochemical properties [82]. Studying the speciation of arsenic or thallium is an analytical challenge and monitoring necessity. Very often, in natural samples, they are accompanied by organic compounds, i.e., active surface compounds, which are found in the extraction or processing of their ores [83]. The toxicity of arsenic and thallium depends on their chemical forms and oxidation states [84]. The thallium occurs in two redox states in water, both of which are toxic [85]. Trivalent compounds, the most toxic form [86], can be present in the suspended matter fraction of polluted water [3]. Arsenic in water occurs mainly as toxic inorganic forms, while the non-toxic organic species of As rarely appear in the dissolved fraction of natural water [87]. The increase in oxidizing potential in water, the activity of microorganisms, and the redox reaction with Mn(IV) or Fe(III) have the effect that As(V) and Tl(I) ions are the dominant forms of these two elements [88,89]. Speciation analysis is, therefore, used to define the real toxicity potential in studied ecosystems. Speciation analysis is usually carried out using (in the case of thallium) liquid chromatography with inductively coupled plasma mass spectrometry (HPLC-ICP-MS) [87,90–93] or electrochemical analysis [94]. Moreover, in the case of arsenic, liquid chromatography separates the forms, which are subsequently detected using spectrometry (AAS, UV-vis) [95] and electrochemical analysis [96].

The exposure of samples to UV-vis radiation has been presented as a factor that negatively influences the speciation of analytes in water samples [63]. The United States Geological Survey (USGS) suggests (in most of its water sampling procedures) keeping the sample in the dark [97]. However, an examination of such advanced analytical procedures shows that they are unreliable when surfactants are present in the sample since these affect the equilibrium of the chromatographic columns and/or lower the sensitivity of the method and produce erroneous results. A partial simplification of the matrix is necessary prior to analysis, but it is not straightforward to apply mineralization since it is known that the classic degradation with oxidizing acids (HNO₃, HClO₄) or 30% hydrogen peroxide supported by microwave energy will disturb the primary speciation. It turned out that selectively ‘muted’ photocatalysis could solve this problem.

Studies on thallium speciation in polluted water containing surfactants require some simplification of organic matter prior to analysis. The pH of the sampled water must be close to the natural value of the water; otherwise, the initial speciation may be altered [98]. A previous study on layers of semiconductors composed in a hierarchically organized manner indicated that the top layer of the catalyst should be made of iron oxide since it enables the pH to be kept around 6 [73]. It is important that samples collected for thallium speciation analysis are doped with DTPA (fixation), which gives a sample with a pH of around 6.2. It should be noted that traces of trivalent thallium in surface water are an effect of the “natural” photooxidation of Tl(I) [98]. Moreover, the addition of DTPA can shift the equilibrium toward the formation of Tl(III). Published data indicated that the irradiation (at 380–800 nm) of water spiked with Tl(I) for 2 h assisted by Fe₂O₃/WO₃/Fe₂O₃ hierarchical

nanostructured layers did not affect levels of Tl(I) (with DTPA and a 100-fold excess of Fe(III)) [61]. As an analytical technique, stripping voltammetry is extremely sensitive to interference from surfactants [99]. This technique was, therefore, used as a type of sensor for the completeness of SDS degradation; it proved that 2 h of heterogeneous photolysis (m) removed SDS compounds and enabled reliable results to be obtained with anodic stripping voltammetry. The results described above, obtained by voltammetry, were consistent with the results obtained by SEC-ICP-MS. Tl(III) reduction under photolysis conditions was in the range of the uncertainty for the measurement of trivalent thallium in any natural matrices due to the natural instability of this species [61].

The heterogeneous photocatalysis is usually used to remove arsenic compounds from water by oxidizing the trivalent form to pentavalent and adsorbing them on the active semiconductor surface, such as Fe_2O_3 [100] or $\text{Fe}_2\text{O}_3\text{@PANI@TiO}_2$ (nanocore-shell) [101]. However, this is a different approach to the efficiency of the oxidation process. For the study of arsenic speciation, based on the published data, sandwich systems with various compositions have been proposed. The best structure with respect to the effectiveness of the degradation process was an active layer of nano-semiconductors composed of three layers ($\text{Fe}_2\text{O}_3/\text{WO}_3/\text{Fe}_2\text{O}_3$) located in an aqueous solution (pH 6). After a photocatalytic process assisted by solar light photolysis (AM1.5, 380–800 nm), the studied samples, which contained inorganic and organic species of As and surfactants (SDS) before organic matter decomposition, were not suitable; additionally, the presence of oxygen in the sample caused the arsenate peak area to be slightly increased after 2 h exposure to sunlight. In the case of arsenic, the crucial point was the saturation of the water samples with argon prior to the photodegradation with sunlight of the active surfactants. Such sample pretreatment led to the decomposition of SDS after 4 h irradiation in the presence of the active layers without any influence on the area and shape peak of the inorganic and organic forms of arsenic [62]. Finally, it can be concluded that the “soft decomposition” or photocatalytic reduction using semiconductors can be proposed as a sample pretreatment before speciation analysis of the water matrix, which makes this technique a very promising addition to the procedures applied in modern water monitoring.

4. The Influence of Photolysis on the Equilibrium in the Water System

The phenomenon of homogeneous and heterogeneous photolysis affects the equilibria of the individual chemical forms of many elements. For example, chromium compounds and the equilibria between the ionic and non-ionic forms of this metal can be particularly difficult to interpret. It is well known that two oxidation states of chromium, Cr(III) and Cr(VI), are stable enough to occur naturally, but they differ in their charge, physiochemical and chemical properties, and biochemical reactivity [84]. The equilibrium (speciation) between the chemical forms of chromium in aquatic ecosystems depends on many factors, such as sun exposure, the content of iron and manganese (oxides/hydroxides), the level of humic acids, and the amounts of calcium minerals (e.g., carbonate and phosphate) present. These complex dependencies will be presented based on our own research. Possible changes in chromium speciation were determined after chromatographic separation of the forms and UV-vis detection. An anion exchange column was used (Hamilton PRP-X100, 250 mm $\times$ 4.1 mm id 10 μm), with a mobile phase of 30 mmol L^{-1} NH_4NO_3 and a flow rate of 1 mL min^{-1} . Signals were recorded at a wavelength of 541 nm for the Cr(III) form and 373 nm for Cr(VI). Before testing, EDTA was added to the solutions (mass ratio to chromium 30:1) to complex the Cr(III) form.

The wavelength range that the speciation system is exposed to is a very important parameter. UV radiation is mainly used in the photodegradation of organic pollutants. In the case of a medium-pressure mercury lamp with a power of 250 W and a maximum wavelength of 254 nm without a catalyst, our results indicated that the method is quite a successful technique for simplification before metal ion determination [21]. This is shown by the comparison of the obtained results for Cd and Pb using ICP-MS and ASV (ultra-trace analysis) in polluted waters (high concentration of surfactants). The RSD reached even as

much as 6% in the case of stripping voltammetry with HMDE (a sensitive technique for the presence of surfactants), while the RSD for ICP-MS (only sensitive when the surfactant content is high) was not higher than 1.4% of the mean values. Additionally, a recovery study produced different recovery values for different UV irradiation procedures. The UV irradiation was not effective enough: the recovery of Cd was 85% and that of Pb 86%. The addition of hydrogen peroxide increased the recovery up to 89% for Cd and 94% for Pb, but the addition of TiO_2 generated a 95% of recovery for both metals. In addition, the sensitivity of quantification increased using a procedure with heterogenous photolysis supported by the presence of TiO_2 [33]. UV irradiation influenced the change in the degree of oxidation of ions such as Cr(III). Our own experience showed that the recorded signal for Cr(III) (HPLC UV-vis, after addition EDTA) after the UV irradiation increased 4.3 times compared to a non-treated sample. Additionally, the appearance of a signal characteristic of Cr(VI) indicated oxidation despite the fixation of the trivalent form of Cr with EDTA [102]. It should be noted that the use of sunlight in this system does not produce such effects if oxygen is removed from the solution. A comparison of the effectiveness of the destruction of SDS under four different photolysis conditions showed that: (1) UV digestion supported by H_2O_2 addition reached 100% (precision of measurements 0.1%) recovery of Pb (tested using ASV determination); (2) using only UV as the decomposing agent provided some decomposition of SDS (recovery 87–88%; precision of measurements 2%); (3) UV decomposition in the presence of WO_3 improved the effects (recovery 95–96%; precision of measurements 0.5%); and (4) sunlight-assisted digestion in the presence of WO_3 was highly effective as the standard method (recovery 99–100%; precision of measurements 0.2%) [5].

It should be pointed out that the UV-vis light occurs naturally, and, therefore, natural photolysis caused by sunlight has an impact on the forms of most compounds in the environment. It is interesting, however, to compare the effects on water samples (mobility, bioavailability) and the degradation of organics in water (self-purification).

The published data show that the presence of carbonate minerals can accelerate or inhibit speciation changes during the irradiation of aqueous samples containing chromium. Changes in the chemical speciation of chromium were determined on the basis of chromatographic separation with UV-vis detection. The data described in the literature indicate that the presence of calcium minerals, such as CaCO_3 and $\text{Ca}_3(\text{PO}_4)_2$, can influence the speciation of chromium in aqueous solutions [103]. According to the published results, compounds of Cr(III) show a strong affinity for materials based on calcium carbonate at pH 5 (egg shells, powdered marble) [104,105], while Cr(VI) adsorbs on the surface of apatite materials at pH 3 [103,106]. These results mean that, in a natural water solution with a pH close to neutral, calcium minerals should limit the oxidation of Cr(III) but should not reduce the amount of dissolved Cr(VI). Our own research confirmed that Cr(III) is adsorbed on CaCO_3 and $\text{Ca}_3(\text{PO}_4)_2$, but, when the processes were performed under UV irradiation, some of the adsorbed Cr(III) was oxidized (after 4 h of irradiation). The transformation of Cr(III) to Cr(VI) in the cases of CaCO_3 and $\text{Ca}_3(\text{PO}_4)_2$ was 30% and 20%, respectively. It should be emphasized that carbonates and phosphates (suspension constituents) may play a role in increasing speciation changes but will not sustain the oxidation of non-toxic chromium forms under natural exposure to sunlight.

The presence of Mn or Fe oxides is the important factor influencing the stability during photolysis. Iron seems to be particularly important. The literature indicates that these particular oxides strongly influence the redox equilibrium of Cr(III)/Cr(VI) in water. In addition to the pH and redox potential, other processes also have an influence on precipitation/dissolution. The concentration of chromium in natural water systems is also controlled by adsorption and desorption reactions. Sorption causes Cr to migrate out of the solution phase to the surface of suspended sediments. Hexavalent chromium can be adsorbed on the surfaces of the particles (which have protruding OH groups) [107].

Literature data show that manganese dioxide, among a few other factors, is able to accelerate the oxidation of Cr(III) to Cr(VI) under natural conditions. The produced Cr(VI)

may adsorb on the surface of the suspended matter, in this case on Mn(IV) oxide [108]. Our study showed that the addition of MnO₂ alone caused an insignificant conversion of Cr(III) (the solution of Cr(III) did not have any addition of EDTA—the reagent used to fix the Cr speciation) [109]), but, if the contact with the solution was 48 h, the recorded signal of Cr(VI) (at 356 nm) increased 1.8 times, while the recorded signal of Cr(III)EDTA (at 541 nm) decreased 1.4 times. It is surprising that the addition of EDTA effectively reduced the oxidation of the trivalent chromium ion at short exposure (UV–vis) times. However, if a semiconductor was present, such as WO₃, a slight reduction in the signal recorded at 541 nm for Cr(III)EDTA was observed. After 1 h, 2 h, and 3 h, the peak area decreased by 4%, 7%, and 12%, respectively. Following the literature, the solution was saturated with argon to reduce the oxidation potential of the solution [62]. These results indicate that heterogeneous photocatalysis affected the water samples even after fixation by the addition of EDTA. This may indicate that organic compounds may limit the photolytic oxidation efficiency of chromium dissolved in water. Some interesting studies indirectly indicate that humic and fulvic acids play an important role in the adsorption of Cr(VI) onto iron minerals. The presence of humic acids clearly reduced the absorption capacity of Cr(VI) on Fe₂O₃ and (to a lesser extent) on magnetite. It can limit the efficiency of the photodegradation process with the use of iron oxides and thus reduce Cr(VI) [110]. However, the mere presence of organic compounds (soil organic material) favors the transformation of Cr(VI) into a reduced form as a result of reduction (phenol and hydroxyl electron donors) and the complexation of the reduced form [111].

Important results were obtained by analyzing the influence of MnO₂ on the stability of Cr(VI) in aqueous solution. Irradiation by UV light over 2 h of a stirred solution of Cr(VI) and MnO₂ (1:10) only reduced the signal recorded from the oxidized form of chromium by 2.2 times. Increasing the amount of oxide by 10 times reduced the area of the signal recorded for Cr(VI) by as much as 14.7 times. These results should be explained by an adsorption of Cr(VI) on the oxide rather than by a reduction because the signal corresponding to the reduced form of chromium was practically not registered. These results are reinforced by the argument that the presence of oxides that can absorb hexavalent chromium will affect the removal of the Cr(III) oxidation product from the solution and accelerate the reaction and its efficiency. MnO₂ is an additive that increases the electrical conductivity (electron or hole) in the matrix material [112]. However, the literature data did not show similar research results or related explanations, although studies using some other photoactive oxides have been published in which some supported photoreduction with adsorption of Cr(VI). The reduction itself was small [113,114], but, if ZnS [113,115] or TiO₂ [116,117] were present in the solution and the adsorption of Cr(VI) and reduction were detected, the scale of the phenomena depends on the acidity of the solution [113].

Iron oxides and hydroxides are natural components of suspensions in surface waters, and iron ions and/or various other iron compounds are found in such waters. These species, after exposure to oxygenation and sunlight, can affect the redox equilibria between the forms of metal ions present [118]. Iron compounds can enter into a redox cycle, which may be accelerated by UV light and organic compounds. This cycle involves the photolysis of Fe(OH)₂⁺ ions, which leads to the release of the Fe(II) ion and the OH• radical. The OH• radical degrades organic compounds, the products of which are other reducing species, which accelerate the reduction of Cr(VI) to Cr(III) and the oxidation of Fe(II) to Fe(III). The efficiency of the process is also influenced by dissolved molecular oxygen, which accelerates the reoxidation of Fe(II), creating a superoxide radical supporting the mineralization of organic compounds. The renewed Fe(III) can re-enter the cycle, causing a further reduction of Cr(VI) [119]. For example, the presence of FeOOH, according to literature data, should cause the adsorption of Cr(VI) and, during 2 h of UV irradiation, a photo-reduction of Cr(VI) at pH 2 gave 100% and at pH 7 gave only 40%. The best conditions for photoreduction were at pH 2. The reduction efficiency was determined on the basis of the decreasing signal from Cr(VI) (spectrophotometric method with the addition of 1,5-diphenylcarbazide) [120].

During an attempt to recreate the photoreduction (UV lamp, pH 3–5) conditions during our own research, signals for Cr(VI) and Cr(III)EDTA were studied (HPLC UV–vis). A decrease in the signal from the Cr(VI) form was noted; however, no signal corresponding to the Cr(III)EDTA form appeared. It was found that, under these conditions, Cr(VI) most likely only adsorbed onto the FeOOH surface. The use of a high-power UV lamp resulted in oxidation rather than reduction. Moreover, we tested xenon lamps emitting solar radiation. The stability of Cr(VI) under photocatalysis conditions in the presence of magnetite (Fe₃O₄; pH 3.8–4.0) was investigated. Additionally, the addition of EDTA as a model complexing agent was examined. It should be noted that the partly dissolved Fe(III) may act as a photocatalyst. The magnetite was immobilized on the wall with a neodymium magnet and the solution was saturated with argon during irradiation to remove reactive oxygen species that could shift the equilibrium toward Cr(VI). The irradiation time was 4 h. The amount of Cr(VI) was reduced in all the tests, the greatest decrease being observed after the addition of EDTA. The stability of the Cr(VI)/Cr(III) system in the presence of EDTA and dissolved Fe(III) was also investigated in the presence of tungsten (VI) oxide. At pH 3.8, after 4 h of exposure to sunlight, there was a reduction of Cr(VI) (several percent); Cr(III)EDTA is stable under these conditions. The efficiency of Cr(VI) reduction in the presence of Fe(III) ions, with (pH 3.2) or without (pH 2.6) the addition of EDTA, was also compared. The removal of the reaction product (complexation with EDTA) from the tested solution caused an equilibrium shift toward the reduction of Cr(VI).

The literature describes the effect of Fe₂O₃ in aqueous solution on chromium speciation under the influence of sunlight. Depending on the dominant form of chromium and the pH, adsorption of Cr(III) and oxidation with a photogenerated electron hole (or homogeneously with a generated hydroxyl radical) or reduction of Cr(VI) with a photogenerated electron of Fe₂O₃ and adsorption of Cr(III) on its surface may take place [121].

Undoubtedly, common iron compounds present in amounts greater than chromium compounds will strongly influence Cr speciation when exposed to light. The obtained results of all these studies can be the starting point for studies on the use of solar photolysis for the remediation of water reservoirs. The reduction of highly toxic Cr(VI) would be a beneficial phenomenon in natural waters, especially if it could be carried out in the presence of chelating ligands.

Another aspect of the stability of the primary physicochemical equilibrium of the chromium system is the use of a photocatalyst in the degradation of surfactants. Photocatalysis is proposed to simplify the organic matrix, but it should be noted that the chemical equilibrium during this process will be changed. Our own study examined the stability of the Cr(III)DTPA complex under various experimental conditions of the photocatalysis of the anionic surface compound SDS. The active layer was made of three layers - WO₃/Fe₂O₃/WO₃. Complexation with DTPA was employed, providing higher stability of the chelate with the +2 and +3 ions [99,122]. There was no statistically significant change in the Cr(III)DTPA signal after 90 min UV–vis irradiation of Cr(III)DTPA. An important point was that it was possible to omit the argon saturation since there was no statistically significant change in the Cr(III)DTPA signals between the solutions saturated with oxygen or argon. Regarding the possibility of self-photocatalysis, it should be noted that the degradation of SDS did not change the appearance of the signal.

5. Summary

The use of heterogeneous photocatalysis is a technique that is constantly being developed. Understanding the mechanisms and factors influencing the equilibria in the aquatic environment, as well as the interaction of light in the presence and absence of various chemical compounds, is important for the development of techniques for the mineralization of organic compounds prior to trace analysis. The use of homogeneous photocatalysis as a pretreatment step is well known and is employed in laboratories prior to the analysis of contaminated water. Supporting these techniques by the presence of semiconductors appropriately selected for the analytical requirements increases the selectivity and limits the

addition of chemical compounds, as well as reducing errors. Heterogeneous photocatalysis was successfully applied to the degradation process in speciation analysis schemes because the indication of the speciation form in the case of many substances is very important, e.g., As(III)/DMA, Cr(III)/Cr(VI). One chemical form of the same element is toxic, and the other is harmless or even essential. Additionally, for the design of photocatalytic materials, various approaches are used to develop new materials with high performance or extended catalytic activity, as well as having a low cost and eco-friendly properties. Photocatalytic processes also have their place in supporting the various stages of chemical or biological wastewater treatment. They will be particularly important in the case of the degradation of biologically active compounds and drugs. Replacing titanium oxide with oxides of other metals, such as Fe or Zn, reduces the risk of introducing, for example, TiO₂ into the biogeochemical cycle. There is still much further work that needs to be carried out in this field.

However, the aim of this publication was to indicate a new application of heterogeneous photodegradation (Table 1) in environmental analysis, and especially in a new subfield of analytical chemistry related to speciation analysis. This is a challenge, especially at the ultra-trace level.

Table 1. The examples of applications of photoactive materials for decomposition of organic matter prior to water analysis or pretreatment.

Application	Semiconductor	Object of Photolysis	Reference
Degradation of dyes	TiO ₂ /Ag	organic dyes and derivatives of benzothiophene	[37]
	N/F/TiO ₂	azo dye and removal of metal ions	[48]
	Fe ₃ O ₄ /TiO ₂ (core-shell system)	Photo-reduction of Cr(VI)	[49]
Wastewater treatment	Fe ₂ O ₃	Photo-oxidation of As(III)	[100]
	WO ₃ /Fe ₂ O ₃	rhodamine B and methylene blue	[60]
Degradation of drugs	TiO ₂	non-steroidal anti-inflammatory	[25]
	TiO ₂	Paracetamol	[26]
Degradation of organic matrix for traces analysis	TiO ₂ /Ag	Simplification of wastewater	[33]
	WO ₃ & Fe ₂ O ₃	Surfactants in natural water	[73]
	WO ₃	Surfactants in natural water	[5]
	WO ₃ /Fe ₂ O ₃ /WO ₃	surfactants in natural water (speciation of TI)	[61]
Degradation of organic matter for speciation analysis	WO ₃ /Fe ₂ O ₃ /WO ₃	surfactants in natural water (speciation of As)	[62]
	TiO ₂ Ag		[74]
	TiO ₂ Au	Photo-reduction of Hg using UV light	[78]
	TiO ₂		[123]

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