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Chapter 11

Monitoring and Management of Anions in Polluted Aqua Systems: case studies on nitrate, chromate, pertechnetate and diclofenac

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11.1 Introduction

Over the past decades, anion toxicity has been widely recognized as a tremendous environmental and health problem. Anion management and sequestration in water bodies has therefore been established as a central issue in most parts of the world. While there is a rather large and heterogeneous group of anions causing these problems, some anionic species are particularly important in terms of their health risks. As a result, tremendous efforts have focused on the removal of these anions from water bodies such as rivers, lakes and groundwater.

The current chapter focuses on four anions, two of which are “conventional” oxoanions (chromate and nitrate), one radioactive (pertechnetate) and one is an organic anion (diclofenac). All these anionic species pose similar risks and can often be treated with similar methods as those used for metal oxoanion-contaminated water and soil.

Nitrate NO_3^- is of prime concern on a global scale, primarily due to problems associated with eutrophication [1, 2]. Chromate CrO_4^{2-} and related ions are common, for example in regions with leather and tanning industries [3, 4]. Pertechnetate TcO_4^- is found in nuclear testing sites and in hospital wastewaters [5-7]. Diclofenac (DCF) is the only non-oxoanion in this series. We chose it as a representative example for pharmaceutical pollutants [8, 9]. These ions are different in that nitrate is based on a non-metal, chromate and pertechnetate are based on a metal and DCF is an organic compound. However, quite some of their properties such as solubility and bioavailability are similar leading to related strategies for water management.

Characteristically, oxoanions with a similar structure, for instance, SO_4^{2-} , NO_3^- , or PO_4^{3-} often coexist. As the concentrations of these individual anions can be quite high and as anion exchange is often unspecific, the sequestration of anions can be more challenging than sequestration of cations [10, 11]. For example, Zhou et al.[12] found that ClO_4^- often coexists with NO_3^- in groundwater at very different concentration levels. Similarly, SeO_4^{2-} coexists with SO_4^{2-} in coal-mining wastewaters,

again in very different concentrations. SeO_4^{2-} and SO_4^{2-} also coexist with NO_3^- in flue-gas desulfurization wastewater.

Additionally, some wastewater contains very high concentrations of some oxoanions (e.g. fertilizer industry wastewater at 1'000 mg/L of NO_3^- or nuclear industries wastewater at 50'000 mg/L of NO_3^-). These high concentrations of one specific anion often hamper an effective sequestration. Additionally, the high solubility and high stability of nitrogen oxoanions makes nitrogen compounds even more challenging to remove from wastewater. As a result, these processes are often energy and cost intensive [13]. For example, coprecipitation shows low potential for NO_3^- removal [14] while conventional ion exchange produces NO_3^- , SO_4^- and Cl^- containing brine that requires further disposal and triggers secondary pollution [15].

Occasionally, very specific properties of a particular oxoanion may also trouble effective sequestration. For example, the high volatility of Tc(VII) (in the form of Tc_2O_7) in wastewater makes the operation of its vitrification or glassification process inefficient [16]. Also, the low selectivity and sensitivity towards competing anions such as Cl^- and CO_3^{2-} , which are present in much higher concentration than pertechnetate, causes many methods for TcO_4^- removal methods to be rather poor.

Similarly, Zhang et al.[17] reported that DCF removal efficiency varies from 0% to 80% in most wastewater treatment plants (WWTPs). Such a large variation may be attributed to multiple factors such as acidity of the water in the WWTP, aerobic/anaerobic ratios, sunlight irradiation and effectiveness of enzymatic cleavage of glucuronide conjugates of DCF. Katarina et al.[18] found that conventional WWTPs are ineffective for DCF removal and a significant fraction of DCF escapes into effluents unchanged.

Designing a selective, efficient and stable means for CrO_4^{2-} reduction or adsorption is challenging as well [19]. One central reason for this issue is that chromium-based anions typically coexist with very high concentrations of CO_3^{2-} , HCO_3^- , SO_4^{2-} , PO_4^{3-} and Cl^- in cooling water and effluents from pigment

and tannery industries. This reduces the overall effectiveness of the adsorbents for CrO_4^{2-} sequestration [19, 20].

Although some progress in the development of effective water treatment materials and processes has been made, a tremendous need for effective, yet cheap and simple, processes for water treatment worldwide remains. This chapter presents recent and promising approaches with a focus on green and sustainable materials and processes. Before discussing these approaches, we will briefly summarize and classify the most common and important oxoanions.

11.2 Common oxoanions: sources, abundance and occurrence

Industrialization and industrial production rely on the use of many hazardous elements and compounds such as heavy metals, metalloids, oxoanions, and derivatives [21-24]. Oxoanions are a particular challenge to water treatment because they are highly water-soluble, very mobile and non-biodegradable and therefore contaminate groundwater, natural aquatic systems and soils [11, 25].

Oxoanions are negatively charged polyatomic ions with the generic formula $\text{A}_x\text{O}_y^{z-}$ where A represents different metal or non-metal elements and O are oxygen atoms. Oxoanions can be both monomeric and polymeric [26, 27]. Oxoanions can be produced from many reactions and processes. Usually industries that generate alkaline wastes mostly through high-temperature processes (thermal waste treatments, metal smelting, fossil fuel combustion) are considered as the common sources of oxoanions [28].

However, not all oxoanions are equally important in terms of availability and contamination. According to Adegoke et al.[27], ClO_4^- , AsO_4^{3-} , SeO_4^{2-} , BO_3^{3-} , CrO_4^{2-} and MoO_4^{2-} are common along with NO_3^- , SO_4^{2-} , PO_4^{3-} and CO_3^{2-} . Han et al.[29] reported that SbO_4^{3-} and TeO_4^{2-} are toxic even at trace levels as well as AsO_4^{3-} and BO_3^{3-} . Besides, MnO_4^- [30], MoO_4^- [31] and BrO_3^- [26, 32] have

often been studied considering their sequestration from industrial wastewater because of their ability to pollute the natural aquatic system.

Furthermore, oxoanions such as VO_4^{3-} and WO_4^{2-} are emerging pollutants, even though their biogeochemistry is still poorly understood. Doğan & Aydın [33] reported that vanadium is released in large amounts into the aquatic environment from glass, rubber, inorganic chemical and pigment industries. Also, the production of phosphoric acid from vanadium-rich minerals results in large amounts of VO_4^{3-} ion extraction and release.

Tungsten has been identified as an emerging environmental contaminant by the United States Environmental Protection Agency (US EPA) [34, 35]. Indeed, Petruzzelli and Pedron [36] showed that WO_4^{2-} is thermodynamically very stable in the environment.

Radiotoxic oxoanions such as TcO_4^- are gaining attention around some parts of the world, especially in regions where production of weapons-grade plutonium and nuclear testing sites are found. Sun et al.[37] showed that TcO_4^- is highly mobile and can be transported into groundwater. Due to its high mobility and toxicity, noticeable attention is also directed towards ReO_4^- sequestration [37, 38]. Ghosh et al.[38] classified ReO_4^- as a rare oxoanion, which is sometimes used as a substitute for TcO_4^- because of the structural likeness of the two anions in terms of hydration energy and charge density. Table 1 summarizes the oxoanions that frequently occur in the aquatic environment and their sources.

Table 1: Important oxoanions as classified by the US EPA.

Element	Oxoanion Species	Uses & Sources	References
Priority Pollutants			

As	AsO_4^{3-} , AsO_3^{3-}	Wood preservation, metal adhesives, textile, pigments, electric plants, pharmaceuticals	[25, 39]
Cr	CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$	Tannery, pigments, electroplating, cooling tower blow-down, chromium plating	[3, 39, 40]
Se	SeO_4^{2-} , SeO_3^{2-}	Glass, electronics, coal combustion, mining, petroleum industries, metal refineries	[41-44]
Sb	SbO_4^{3-}	Mining, smelting, waste incineration, fossil fuel combustion	[31, 41, 45]
Contaminant candidate list (CCL4)			
Cl	ClO_3^-	Paper & pulp, flour & oil processing, leather de-tanning, cleaning agent production	[26, 46, 47]
Mo	MoO_4^{2-}	Stainless steel production, metallurgy, pigment, catalyst industries	[25, 31, 46, 48]
Mn	MnO_4^-	Iron & steel alloy manufacturing, bleaching & disinfection by-product, catalysis	[46, 47]

Te	TeO_4^{2-} , TeO_3^{2-}	Gold mining, deep sea hydrothermal vent systems	[46, 49, 50]
V	VO_4^{3-}	Photography, glass, rubber, ceramic, mining, oil refining	[25, 46, 48]
Emerging contaminants			
Cl	ClO_4^-	Solid rocket fuel propellant, pyro-techniques, explosives, fireworks, munitions	[26, 32, 51]
W	WO_4^{2-}	Military sites, fertilizer production, golf clubs, heat sinks, metal wires, turbine blades, television sets	[25, 35]
Most Abundant Oxoanion Species			
P	PO_4^{3-} , PO_3^{3-}	Food & beverage industry, agriculture, fertilizer, detergent production	[27, 52]
S	SO_4^{2-} , SO_3^{2-}	Beam-house of tanning, fertilizer, chemical, textile, soap, paper	[53-55]
N	NO_3^- , NO_2^-	Nitrogenous fertilizer production, wastewater disposal, agricultural runoff	[1, 2, 26, 47]

Further hazardous pollutants			
B	BO_3^{3-}	Glass manufacturing, flame retardants, soap & detergent production	[25, 47]
Br	BrO_3^-	Textiles, flour milling, beer production, fish paste production	[26, 32, 47]
Tc	TcO_4^-	plutonium production, military tests and waste, fission material production, radiopharmaceutical tracer	[56]

Furthermore, besides conventional oxoanions as defined above, organic drugs and metabolites bearing anionic groups such as carboxylate or sulfonate have also caused increasing concern. Their concentration has grown due to increased release from medical and pharmaceutical wastes to open waters and ground water in North America and Europe [57-59]. Low-cost over-the-counter drugs like the non-steroidal anti-inflammatory drugs (NSAIDs) Ibuprofen, Diclofenac, Naproxen and Indomethacin have therefore been identified as emerging contaminants [60]. Because of the heavy discharge by households, hospitals, pharmaceutical industries and agriculture, Diclofenac is on the “Watch list of the EU Water Framework Directive” [9, 57]. As a result, DCF has therefore been studied and reviewed far more than 400 scientific articles in the previous two decades [9].

11.3 Oxoanions in aquatic system: public health and environment

In natural environments, oxoanions exist in a variety of species. Speciation depends on numerous factors including pH, electrochemical potential (Eh), redox conditions, electrolyte compositions,

temperature and microbial activity [26, 61]. For example, SO_4^{2-} is thermodynamically more stable than SO_3^{2-} at pH 6.5-8.5 and Eh 0.1-0.4V [26]. Also, SO_4^{2-} can be protonated at sufficiently low pH yielding HSO_4^- ; both sulfate and sulfuric acid are major drivers in the formation of atmospheric aerosols, which have been held responsible for climate change, adverse public health effects and natural sulfur cycle misbalance [62]. Above 600 mg/L, the presence of SO_4^{2-} noticeably changes the taste of drinking water and causes laxative effects. Therefore, for industrial effluent and mine drainage, a maximum concentration of 250 – 1000 mg/L SO_4^{2-} has been set [53]. Depending on the pH and concentration, different species such as HSO_3^- , $\text{S}_2\text{O}_5^{2-}$, SO_3^- and dissolved SO_2 exist in the aquatic environment [63].

Nitrate is another very common and highly soluble water contaminant. It naturally occurs in the nitrogen cycle and is the most stable form of N for oxygenated systems [1]. In contrast, NO_2^- preferably exists in reducing environments and can be oxidized to NO_3^- . Gee Chai et al.[64] reported that one common biological NO_3^- formation process includes *Nitrosomonas* and *Nitrobacter* species. First, ammonium is oxidized to NO_2^- by *Nitrosomonas* and *Nitrobacter* then further oxidizes NO_2^- to NO_3^- .

A high NO_3^- concentration in surface water increases algal growth, causes eutrophication and extinction of aquatic life [2, 65]. Vegetables, meat and drinking water are vectors for both NO_3^- and NO_2^- uptake by humans and animals. The World Health Organization (WHO) has categorized NO_3^- as a major drinking water contaminant with a maximum permitted limit (MPL) of 50 mg/L because it causes stomach cancer in adults and blue-baby syndrome in infants [66].

NO_2^- is considerably more toxic than NO_3^- and causes respiratory tissue hypoxia and cell failure. In light of this, the European Food Safety Authority (EFSA) has set the MPL of 10 – 500 mg/kg and 50 – 175 mg/kg for NO_3^- and NO_2^- , respectively for different types of food [65]. Rajmohan et al.[13] and Mohseni et al.[15] showed that high concentrations of NO_3^- in surface and groundwater is an acute problem in the UK, Europe, Japan, China, Saudi Arabia, Australia, North America, Morocco, western

Iran and India, among others. Bijay et al.[67] suggested that developing countries in Asia or humid tropics of Africa are potentially more prone to NO_3^- pollution due to the high amounts of nitrogen-containing fertilizer used in agriculture. The study also revealed that countries with lower fertilizer use in north, central and west Africa (where soils are mostly aridisols and likely to stay dry almost all year) are less affected by NO_3^- pollution.

Besides non-metal-based oxoanions, a wide variety of metal and metalloid oxoanions are found in the aquatic system in large quantities with a diverse speciation. For example, chromium is a toxic metal known to form many oxo species. Its most important oxidation states are Cr(III) and Cr(VI) [68]. Cr(III) is an essential nutrient for cell function and the metabolic system, relatively stable and less of a threat for public health and environment [69]. On the other hand, Cr(VI) affects the water ecosystem and the plant and animal kingdom adversely due to its high solubility mobility and lethal character [3]. Considering the different forms of Cr(VI) (e.g. HCrO_4^- , CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, H_2CrO_4), HCrO_4^- is the dominant species at a pH 2.5 – 5 [70]. Rakhunde et al.[68] stated that the chances are higher to find HCrO_4^- and CrO_4^{2-} in typical surface water when the concentration of chromium is less than $5\mu\text{g/L}$. HCrO_4^- and CrO_4^{2-} are the prevalent species between pH 6 and 7, whereas concentrated Cr(VI) likely contains $\text{Cr}_2\text{O}_7^{2-}$ in highly acidic media [71]. Liu et al.[72] reported the presence of HCrO_4^- at lower pH and the transformation to CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ with increasing pH.

These anions can bioaccumulate and cause damage to aquatic organisms such as mucous secretion, irregular swimming, discoloration, erosion of scales, increasing mortality and disorder in osmoregulatory functions [73]. Generally, Cr(VI) is taken up by the human body through the respiratory tract and skin, leading to teratogenicity, mutagenicity, carcinogenicity, neurotoxicity, liver and kidney failure, respiratory problem, skin disease and many other issues [71, 73, 74].

Several studies suggest that plants also take up CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ and subsequently suffer from lower plant yield, stem growth, root growth, germination and photosynthesis [74-76]. Probably chromium also percolates through soils and undergoes various changes such as oxidation, reduction,

precipitation and dissolution in the presence of dissolved oxygen and MnO_2 , and ultimately contaminates the groundwater [74]. As a result, Cr(III) and Cr(VI) compounds are major contaminants and regulated by the WHO and US EPA. For drinking water, a maximum 0.05 mg/L is permissible by WHO while USEPA allows only 0.01 mg/L [70].

Like chromium, vanadium forms a wide variety of oxoanions. A substantial increase of vanadium compounds in water and soil and its potential toxicity is currently raising concerns around the world [25, 77]. According to the Forum of European Geological Surveys (FOREGS) the vanadium concentration in European soil ranges from 1.28 to 537 mg/kg [78]. Vanadium has been adopted in both US EPA Contaminant Candidate Lists (CCL 3 & 4) [77] based on the fact that high vanadium exposure can irritate the mucous membrane and lead to gastrointestinal disturbance, anemia, cough and bronchopneumonia, among others [33, 79]. Generally, a pH above 3 was recognized best for the formation of various monovanadate (e.g. $\text{VO}_2(\text{OH})^{2-}$, $\text{VO}_3(\text{OH})^{2-}$, VO_4^{3-}), polyvanadate (e.g. $\text{V}_2\text{O}_6(\text{OH})^{3-}$, $\text{V}_2\text{O}_7^{4-}$, $\text{V}_3\text{O}_9^{3-}$, $\text{V}_4\text{O}_{12}^{4-}$) and decavanadate (e.g. $\text{V}_{10}\text{O}_{26}(\text{OH})_2^{4-}$, $\text{V}_{10}\text{O}_{26}(\text{OH})^{5-}$, $\text{V}_{10}\text{O}_{28}^{6-}$) species [80].

Recently, an increasing use of tungsten has raised interest and concern. Although tungsten appears inert and less toxic, it impedes the growth of nitrogen-fixing bacteria and plants and is toxic for fish and other aquatic species [81]. Moreover, the death of ryegrass and red worms [25] and other observations make W an emerging contaminant [35]. Tetrahedrally coordinated WO_4^{2-} is the dominant form under neutral to alkaline conditions, while under acidic condition tungsten forms polytungstates like $\text{W}_7\text{O}_{24}^{6-}$ and $\text{H}_2\text{W}_{12}\text{O}_{43}^{10-}$ [25, 81].

Similar to tungsten, rising levels of tellurium oxoanions in seawater, mining areas and industrial areas have attracted enormous attention for quite some time. Tellurium is perceived as the least available stable element in the environment and may exhibit various oxidation states [82, 83]. Harada and Takahashi [84] found HTeO_3^- as main species at pH 2 - 4 and Eh 0 - 0.4 V. In contrast, HTeO_4^- , TeO_3^{2-} and TeO_4^{2-} are the dominant species at neutral to alkaline condition (pH 7.5 – 12) with an Eh

range of 0.1 – 0.5 V [84]. Their solubility increases with temperature and alkalinity and Te(IV) is ten times more toxic than Te(VI) [84]. Tellurium often stems from the rubber and metal industry. Further transport causes bioaccumulation in kidney, liver, heart and other tissues showing acute toxicity particularly in young children [85]. Furthermore, microorganisms and bacteria suffer from TeO_3^{2-} even at concentrations as low as 1 $\mu\text{g/mL}$ [86].

A completely different source of pollution, production of weapons-grade plutonium, nuclear fuel reprocessing and research sites have been generating nuclear waste for decades. Among others, this produces radioactive technetium, a common surface and groundwater contaminant in nuclear testing sites [87] such as the United States Department of Energy (US DOE) sites [88]. Moreover, $^{99\text{m}}\text{Tc}$ is also used as a radiotracer in clinical settings [89].

Multiple studies specified that technetium mostly occurs as Tc(VII) in the form of TcO_4^- under atmospheric or moderately oxidizing conditions [56, 87]. Under moderately reducing and anaerobic conditions, $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ and TcS_2 are the dominant species as Tc(IV). Due to high solubility and mobility, TcO_4^- gets picked up by plants and thus accumulates in the food chain using the same mechanism as SO_4^{2-} and PO_4^{3-} [56]. Persistent accumulation of TcO_4^- in lung tissue may initiate significant risks, where technetium tainted dust or vapor inhalation promotes the chance of lung cancer and associated maladies [90]. Finally, TcO_4^- uptake causes cell death for blue-green algae [91] and the same study also finds TcO_4^- responsible for constraining photosynthesis and suffocation for many organisms.

Besides these purely mineral oxoanions, organic anions represent another class of emerging contaminants. As a representative example, the presence and treatment of Diclofenac (DCF), a common pain-killer, in water has been thoroughly investigated. DCF and related compounds are widely spread over the globe. DCF was identified as ubiquitous organic pollutant in various water bodies and it was therefore included in the EU watch list of emerging contaminants [92].

The fate of DCF has become a significant concern since most of the DCF (almost 75%) escapes the WWTPs unaltered and therefore contaminates aquatic environments and soil both in its parent and metabolite form [9, 93, 94]. DCF has also been detected in drinking water in many countries including USA, Japan, Germany, France, Spain, Sweden or Taiwan [8, 9]. Long term DCF exposure to the human body may cause gastrointestinal bleedings, renal papillary necrosis, peptic ulceration, hepatotoxicity and renal failure, among others [95]. Furthermore, DCF is responsible for renal failure in birds leading to their death [96]. Liver, heart, pulmonary and renal lesions in vultures, mice, rats and many other animals have also been linked to DCF [96-98].

11.4 Current approaches to oxoanion sequestration

11.4.1 Nitrate as an example of a non-metal-based oxoanion

Multiple solutions to address the problem of nitrate removal and reduction exist. As stated above, nitrate is a severe environmental problem [1, 2, 13, 15, 65, 67] and there is thus a need to effectively treat water contaminated with nitrate. These developments and approaches have been reviewed [99-107] and we will thus focus on a series of examples to illustrate the breadth of these approaches. They can be broken down using a materials perspective, but, unlike in the case of Cr (see below), the variability of these different approaches seems somewhat broader and less centered around one or two core concepts.

Biomass and carbonaceous materials

Biomass, biochar and other carbonaceous materials have been studied for nitrate removal. For example, Heaney et al.[108] have shown that biochar can be modified with suitable components to improve nitrate sorption efficiency. They used low molecular weight organic acids (citric, malic, oxalic acids) to protonate the biochar which was otherwise not effective for nitrate removal.

According to the authors, surface protonation provides enough positive charges on the biochar to remove nitrate by electrostatic interactions.

Exploiting waste materials that would otherwise be burned, Pan et al.[109] have modified biogas residues with amine and ammonium groups. The materials have sorption capacities up to ca. 62 mg/g of nitrate. Moreover, the materials show an excellent reproducibility in recycle experiments. In a similar approach, Zhao et al. used agrowaste (corn cobs, peanut shells, cotton stalks) to produce carbonaceous adsorbents, but the highest capacity reported by these authors is around 15 mg/g.

Machida et al.[110, 111] showed that PAN and Rayon fibers can be transformed to carbonaceous adsorbents via steam activation or solvent treatment and subsequent carbonization. The two studies report closely related approaches aiming at the introduction of nitrogen into the carbonaceous fiber materials. Nitrogen doping is intended to produce amine and ammonium sites that would then facilitate nitrate uptake via ionic interactions.

Taoufik et al.[112] used activated carbon and statistical analysis to evaluate the performance in nitrate removal with the highest fraction of nitrate removal being ca. 96%. While this work provides an interesting approach to minimize the actual number of experiments, there is essentially no information on the type of activated carbon used by the authors. As such, a valorization of the work is rather difficult.

An extension to some of the work above, Yin et al.[113] have fabricated Mg-Al modified biochars from soybean waste. The addition of Mg and Al produces MgO, AlOOH and MgAl₂O₄ within the biochar matrix. Addition of the inorganic components increases the surface areas up to ca. 350 m²/g and the authors found a maximum nitrate adsorption capacity of ca. 40 mg/g. One question that was not addressed in this study, however, is the loss of Al(III), which may pose environmental risks in itself.

In a somewhat different approach, Oyarzun et al.[114] demonstrated that carbon electrodes can (1) be modified with suitable surfactants and (2) the application of suitable potentials to the electrodes

further support the adsorption or desorption of nitrate due to mostly electrostatic interactions. This is an interesting approach because it enables an effective and simple adsorbent regeneration, in principle even in situ, Figure 1.

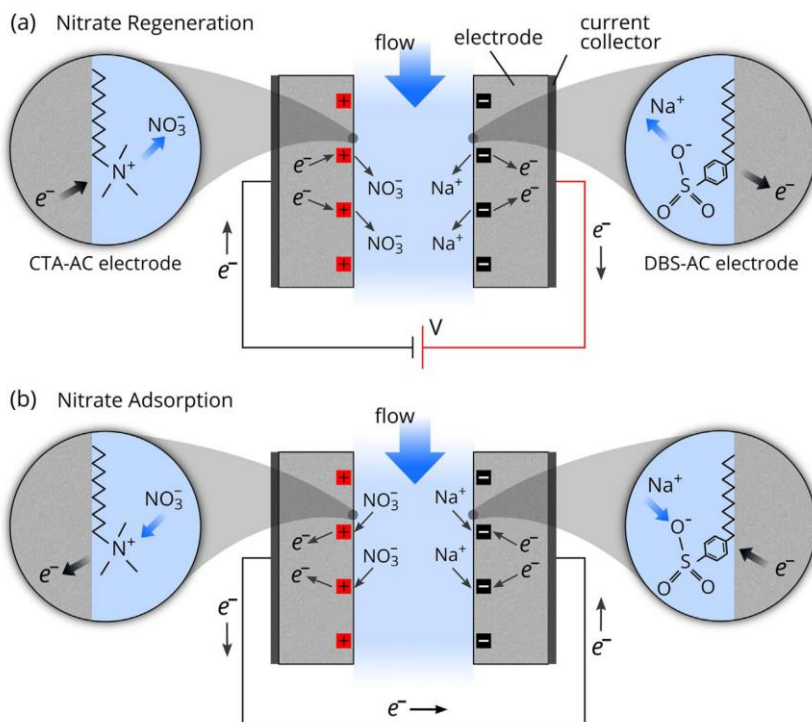


Figure 1. Concept of nitrate removal using carbon electrode adsorbents. Figure reprinted from ref.[114] with permission.

Composites

Viglasova et al.[115] investigated the synthesis and properties of biochar/montmorillonite composites for nitrate removal. The biochar was produced from bamboo and the main data showed that addition of montmorillonite (yielding a carbon/mineral composite) more than doubled the adsorption capacity compared to plain biochar.

Cui et al.[116] used carbon materials obtained from crude oil waste modified with chitosan and iron oxide to remove nitrate. The resulting hybrid spheres show an interesting adsorption behavior: over

five recycling experiments nitrate essentially shows the exact same rates of removal. In contrast, phosphate, which was also studied, is removed less effectively as the recycling continues. The authors propose that the interactions that are responsible for nitrate and (dihydrogen)phosphate removal are comprised of electrostatic interactions between various charged groups on the surface, but also through hydrogen bonding and via exchange between nitrate or phosphate and surface-adsorbed anions such as chloride.

Again using chitosan, Zarei et al.[117] synthesized Ag-TiO₂/γ-Al₂O₃/chitosan nanocomposite thin films. The films exhibit some porosity and their main principle of action is not adsorption but photocatalytic nitrate reduction. The catalyst removes ca. 50% of nitrate at catalyst doses of 1 g/L. Competing anions reduce the activity of the catalyst and the highest activity was reported at pH over 7.

Using poly(ethylene imine) (PEI) rather than chitosan, Suzaimi et al.[118] modified porous rice husk silica with polyamine chains to enhance nitrate adsorption. The interesting feature of these materials is that the underlying silica matrix has an MCM-48 structure and therefore rather high surface areas of over 700 m²/g. Being porous, the materials contain large fractions of PEI after the modification step. This reduces the surface area but enhances anion uptake through protonation and hence electrostatic interaction. Indeed the authors reported a nitrate sorption capacity of ca. 40 mg/g for neat rice husk silica and about 80 mg/g for the PEI-modified material. Using synthetic MCM-41 rather than biogenic MCM-48 type structures, Ebrahimi-Gatkash et al.[119] produced amino modified mesoporous materials with nitrate sorption capacities up to 38 mg/g. Moreover, Phan et al.[120] used an analogous approach by modifying rice husk ash with triamines. The resulting materials showed a very high adsorption capacity of over 160 mg/g and showed a reasonable recyclability over 10 cycles. Karthikeyan and Meenakshi [121] reported the performance of magnetite/graphene oxide/carboxymethylcellulose nanocomposite beads prepared by a precipitation technique, Figure 2. The beads are rather uniform in size and show good adsorption capacities for phosphate and nitrate.

The highest capacities were found at around neutral pH at ca. 40 mg/g (even though the abstract and conclusion states roughly twice this value).

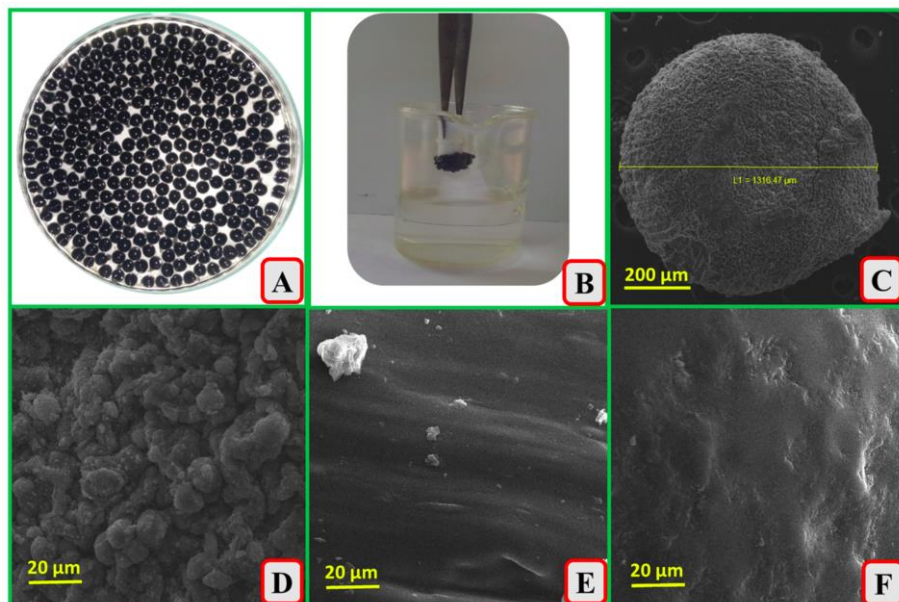


Figure 2. A, B) Photographs of porous spheres for nitrate removal, C-F) scanning electron microscopy images of beads and bead surface. Figure reprinted from ref.[121] and used with permission.

Yang et al.[122] describe a bifunctional adsorbent based on $\text{Fe}(\text{OH})_3$ and an amine-modified polystyrene resin. The composite provides a large number of adsorption sites and the authors report that there is essentially no competition between nitrate and phosphate. Similar to another study [116] the authors found that the adsorption capacities of phosphate are reduced over ten recycle experiments while the nitrate capacity essentially remains the same. High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) along with elemental mapping further shows that both nitrogen (i.e. amine modification and nitrate) and phosphorus (i.e. phosphate) are homogeneously distributed throughout the materials, Figure 3.

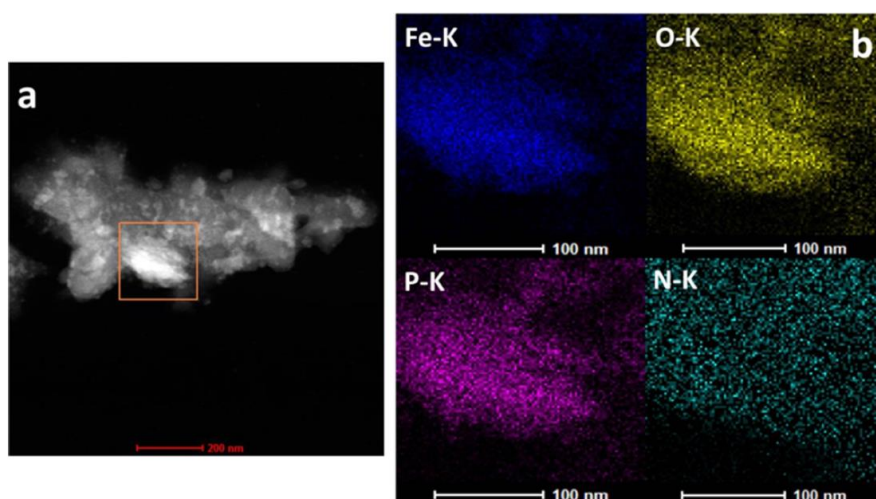


Figure 3. (a) STEM-HAADF image and (b) elemental maps of Fe, O, P, and N in the yellow frame in panel (a) of adsorbent prepared by Yang et al. Figure reprinted from ref.[122] and used with permission.

Using poly(amido amine) dendrimers rather than PEI to modify graphene oxide, Alighardashi et al.[123] produced powders with a flake-like morphology. The authors claim that the nitrate removal is essentially independent of pH between pH 3.5 and 10.5 but as the data are given without error estimations this is rather hard to quantify.

Jaworski et al.[124] used montmorillonite modified with various ammonium surfactants to (1) introduce positive charges into the inorganic host and (2) to open up the montmorillonite layer structure to improve the accessibility of internal sites. The importance of the interlayer opening is illustrated by the fact that in most cases no removal of nitrate was observed with short chain surfactants while with longer chain surfactants the exchange/removal capacity increased.

Finally, Omorogie et al.[125] described papaya seed/clay hybrids for the removal of nitrate. This work is based on earlier work [126] establishing that papaya/clay hybrids are effective for heavy

metal removal but the more recent publication [125] demonstrates that these composites are in fact useful and effective for removal of a wide range of pollutants including anions.

Inorganics

In a very elegant study, Wang et al.[127] demonstrated that halide alloying in BiOX (X = Cl, Br) can be used to optimize the photocatalytic reduction of nitrate. The authors performed an in-depth analysis of the materials including the photocurrent generated upon irradiation and supported these measurements with analyses of defects. In particular, the authors showed that oxygen vacancies on the surface of the nanosheets are key reaction sites that favor the adsorption and reduction of nitrate, Figure 4. Overall this is a very interesting fundamental study providing access to further concepts for catalyst design for nitrate reduction.

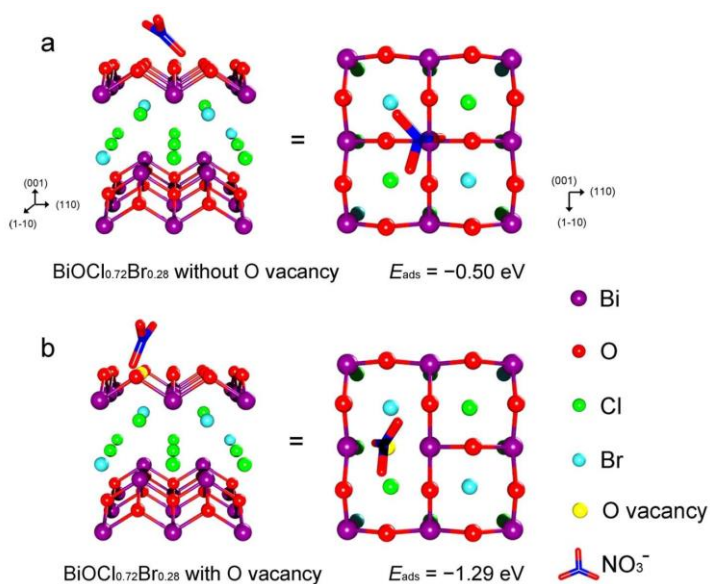


Figure 4. Schematic representations of an NO_3^- ion adsorbed on the surface of $\text{BiOCl}_{0.72}\text{Br}_{0.28}$ (a) without and (b) with O vacancies (computational results). Figure reprinted from ref.[127] and used with permission.

Li et al.[128] demonstrated highly effective photocatalytic reduction of nitrate with an inorganic/inorganic hybrid catalyst made from Pd/In clusters with different stoichiometries supported on FeO_x. Using a combination of experimental and theoretical methods, the authors demonstrated that the key step in the catalytic process is an electron transfer from the Pd/In cluster to the FeO_x support. This electron transfer is supposed to generate positively charged sites on the clusters promoting the adsorption of nitrate and hydrogen to then favor the catalytic nitrate reduction reaction at these sites.

Geng et al.[129] also studied the photocatalytic reduction of nitrate but using a more conventional material, AgCl on TiO₂ nanotubes. The authors demonstrated that the chemical nature of the hole scavenger (formic acid vs. several other compounds) drastically affects the performance of the overall reaction. Moreover, the authors also showed that with increasing irradiation time AgCl is transformed to Ag(0) nanoparticles that can clearly be distinguished in transmission electron microscopy analysis. Recycling experiments showed a reproducible performance over four cycles similar to other data [128] albeit with longer times needed for nitrate reduction.

Along the same general concept, Adamu et al.[130] showed that Cu-enriched TiO₂ is able to degrade both nitrate and oxalic acid at the same time. The authors highlight the importance of the thermal treatment as only some of the materials showed the necessary photochemical activity while others did not show any activity. In particular the presence of Cu₂O appears to be a key requirement for proper reaction of the catalyst with nitrate. The authors assign this to the redox behavior of the Cu(I) ion which is deemed necessary for the electron transfer reactions.

Khatamian et al.[131] developed an ultrasound-assisted route towards Fe₃O₄/bentonite hybrids. The materials effectively remove nitrate from aqueous solution and the adsorbents can be separated from the liquid phase by applying a magnetic field. In spite of this, it is difficult to compare the data to other work because the authors do not provide adsorption capacities.

Chu et al.[132] synthesized ammonium-modified zeolite Y by attaching aminosilanes to the zeolite solids. The resulting powders effectively remove nitrate, ammonium and phosphate from aqueous solution and the materials can easily be recycled via washing with aqueous NaCl. In a similar study, Wu et al.[133] used LaCl₃ or hexadecyl trimethylammonium bromide-exchanged NaY zeolite. Especially the La-modified zeolite showed high nitrate removal capacities.

Rezvani and Taghizadeh [134] used a simple raw material, clay (although they unfortunately did not specify the exact type of mineral), that was ground to below 150 µm in diameter and then hand formed into small spheres of ca. 5 mm in diameter that were allowed to dry. A second type of material was prepared from montmorillonite clay with particle sizes below 20 nm. Both materials were heat treated at 1000 °C to produce ceramic spheres. Adsorption experiments showed that nitrate is removed from solution by these particles but as the authors do not provide errors on their experimental results, it is not possible to compare the performance of the two materials.

Resins and Gels

One of the major aspects in water treatment is cost. Duan et al.[135] have therefore studied the use of commercial trimethylamine-modified poly(styrene) (PS) anion exchange resins for nitrate removal. The authors identified a number of aspects that are critical for proper nitrate removal from nitrate-rich groundwater. In particular, the presence of sulfate and bicarbonate was reported as a major influence on the performance of the resin and the authors assigned the improved performance in some cases to the specific sulfate/chloride or bicarbonate/chloride ratios present in the system. Li et al.[136] followed the same approach and again triethyl ammonium groups on PS resins were found to be the most efficient moieties for nitrate removal. Moreover, these authors also stated that poly(acrylic) resins did not perform as well as the PS-based resins.

Li et al.[137] studied magnetic cationic hydrogels based on (3-acrylamidopropyl) trimethylammonium chloride producing a highly charged hydrogel network. The magnetic properties

were introduced into the system by addition of $\gamma\text{-Fe}_2\text{O}_3$ during the synthesis. The authors report a considerable pH dependence and the highest nitrate sorption capacity of ca. 95.5 mg/g was observed between pH 5.2 and 8.8. Using a related approach, Sun et al.[138] synthesized gel adsorbents from an alkylammonium acrylate that are able to remove nitrate from real secondary treated waste water. Kalaruban et al.[139] described the combination of adsorption and electrodiffusion. A stainless steel mesh box was filled with Dowex ion exchange resin and a piece of copper was used as the counter cathode. The combination of applying a potential to the steel/copper pair with the presence of the Dowex resin in the vicinity of the steel mesh box provides a better nitrate removal efficiency than either Dowex or potential difference alone. The authors also highlighted that there is a strong dependence on the performance from the electrode distance and the applied potential. The optimum settings are a distance of 1 cm, a potential of 3 V and a temperature of 30 °C.

Using a membrane approach, Maghsudi et al.[140] showed that pressure and the combination with a column setup can greatly enhance nitrate removal. The authors report removal of over 90% of nitrate using appropriate combinations of pre-treatment and membrane separation. Activated carbon improves the performance of the process.

Khalek et al.[141] investigated chitosan/gelatin/poly(2-(N,N-dimethylamino) ethyl methacrylate) mixed gels along with different modifications of this combination. The gels were prepared by gamma irradiation and various modifications, such as the reaction with thiourea to provide thiol groups was investigated. The authors highlight that the presence of SiO_2 improves the adsorption capacity compared to the materials prepared without silica. While the authors do not provide detailed insights as to why this is the case, they do provide thermodynamic information allowing for estimation of the individual components to the overall sorption process.

Various processes

Finally, there are a few approaches that cannot be grouped in one of the above sections. First, Zhang et al.[142] reported a nitrate-dependent ferrous oxidation process. This process involves bacteria and

the authors initially attempted to couple nitrate reduction with As(III) oxidation to simultaneously remove nitrate and arsenic from solution. However, the authors found a rather strong pH dependence of this coupled process and the reaction did not work properly in all pH regimes. Consequently, the authors employed a modified process with a separation of the two steps whereby first nitrate is reduced by the bacterial process followed by removal of the arsenic.

Saha et al.[143] fabricated a biofilm containing three bacterial strains that, in combination, simultaneously remove nitrate and phosphate to levels considered safe for drinking water. The authors highlighted the fact that the combination of several bacterial strains in the bioreactor is necessary, as individual strains are not able to individually perform the same reactions at the same level. According to the authors “This is by far the fastest, energy efficient technology for wastewater treatment which adds to sustainability of irrigation and aquaculture and reduces dependency on synthetic fertilizers and potable water for irrigation.”

Gao et al.[144] introduced a new ultrafiltration process for simultaneous removal of nitrate and phosphate. The key component in this process is a tailor-made membrane based on amorphous zirconium hydroxide, quaternary ammonium salts and poly(vinylidene fluoride). Membranes were fabricated by phase inversion and had thicknesses on the order of 80 to 250 μm . According to the authors, the high nitrate and phosphate removal efficiencies are due to the high ion exchange capacities and the high number of surface hydroxyl groups introduced via the amorphous zirconium hydroxide.

Kalaruban et al.[145] used a combination of adsorbents (Dowex resins, amine-grafted corn cobs, amine-grafted coconut shells) in combination with a semi continuous membrane process. Essentially the method involves adsorption of the contaminant onto the adsorbents followed by membrane diffusion and separation of the purified water phase using a pump setup. The process is continuous in the sense that the water feed and effluent can be run in continuous mode but the adsorbents must be exchanged once their capacity is reached.

Finally and using a completely different approach, Hosseini and Mahvi [146] used controlled freezing for nitrate removal. The authors highlight the fact that freezing is among the simplest and most readily available processes even to non-expert persons. Moreover, their data suggest that a single freezing-melting run may in many cases be sufficient to lower the nitrate concentration to below the WHO limits considered safe for drinking water.

11.4.2 Chromate as an example of a metal-based oxoanion

As detailed in the introduction, chromium, especially Cr(VI), poses significant environmental threats and health hazards [71, 73-76]. As a result, there is a need for chromium removal from water bodies and drinking water sources. Given the fact that a large fraction of chromium contamination occurs in developing countries, these water treatment methods must be cheap, readily accessible, and preferably be based on local resources. The following sections illustrate some of the developments that have been put forward over the last years. These developments have also been reviewed [147-152].

There have been numerous suggestions as to how Cr can be removed from water by adsorption. From a materials perspective, these can be grouped into (1) biomass and carbon based adsorbents, (2) composite materials, typically organic or carbon/inorganic composites, (3) inorganic materials, and (4) polymer resins and gels. Sometimes these materials also contain moieties that provide photocatalytic or redox activity to further enhance the materials performance beyond mere adsorption.

Biomass and carbonaceous materials

Biomass is among the most interesting pools for raw materials because there is a large variety of biomaterials that is accessible worldwide. Moreover, biomass comes in a virtual unlimited supply and depending on the region, different biomasses are available. There is thus no need for long transport chains and often, biomass is available as waste material that is not used otherwise. There is thus no competition with, e.g., food supplies.

As a result, biomass and carbonized biomass have also been studied for chromium removal [149, 151, 152]. To highlight a few recent approaches, we will focus on some studies that have appeared in the recent past and put forward interesting examples of this general approach.

Erabee et al.[153] studied the use of garden waste for the generation of activated carbons. A pool of agricultural waste was treated with $ZnCl_2$ as an activating agent and fixed bed studies showed that Cr(VI) can be removed from aqueous solution using the resulting materials. Among others, the authors showed that flow rates do not significantly influence the performance of the materials. However, increasing the column length in fixed bed experiments drastically improved the overall removal effectiveness from 42% to 95% of Cr(VI) being removed when the bed depth of the activated carbon was increased from 3 to 7 cm.

Using a somewhat unusual biomass resource, *Sterculia villosa Roxb.*, Patra et al.[154] prepared sorbents for Cr(VI) using a combination of grinding the raw materials to very small particle sizes (below 200 nm), acid activation and thermal treatment. The materials have surface areas of 700-800 m^2/g and Cr uptake could directly be shown on dry samples using energy dispersive X-ray spectroscopy. The authors also reported a strong pH dependence of Cr adsorption, with an essentially 100% removal efficiency at low pH (2-3) and ca. 10-20% at pH above 7.

Pakade et al.[155] studied macadamia nut shells as a source for activated carbon. Macadamia is farmed in large volumes in Australia, Hawaii, and South Africa and macadamia nut farming produces large amounts of nut shells that are essentially unused agro waste. The activated carbon was produced by a steam activated heat treatment at 900 °C producing carbons with surface areas over 900 m^2/g . These materials have a Cr(VI) adsorption capacity of 23.3 mg/g at pH 2. According to the authors, the process also involves some reduction of Cr(VI) to Cr(III).

Using an approach that may not currently be accessible to mass applications due to high cost, Mondal et al.[156] presented an interesting fundamental study on how reduced graphene oxide can be functionalized with guanidine groups to enable Cr(VI) removal, Figure 5. The authors performed an in-depth characterization of the materials and demonstrated that 139 mg/g maximum adsorption

capacity in acidic conditions and 51 mg/g can be reached in acid-free conditions. Importantly, these result can be achieved at low adsorbate concentrations and increase even further at higher concentrations of 400 ppm to reach 173 mg/g adsorbent. Clearly, while this approach is not suitable for large scale applications, the general idea is certainly interesting for further technology development.

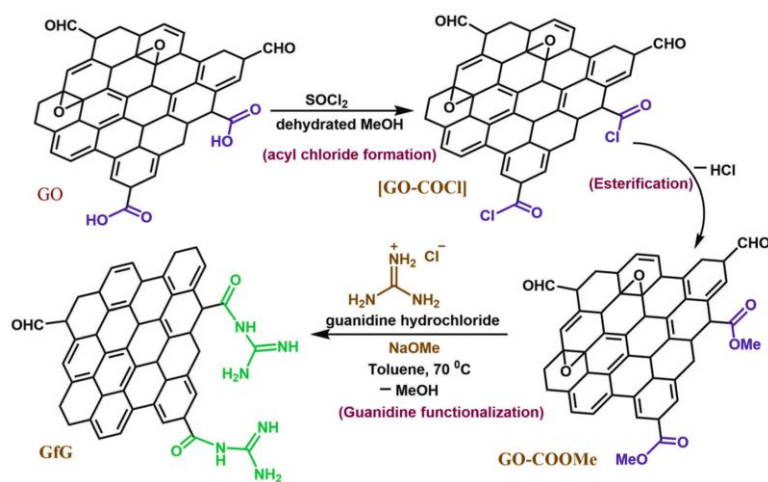


Figure 5. Synthesis of guanidine-modified graphene oxide for chromate sorption. Reprinted from ref. [156] with permission.

Using a closely related approach, Nkutha et al.[157] have made graphene-based sorbents by modification of graphene oxide with amino- and mercaptosilanes providing materials with $-\text{NH}_2$ and $-\text{SH}$ functional groups suitable for metal binding. The main outcome of the article is the observation that, analogous to the work by Mondal et al.[156], the highest adsorption efficiencies were observed at pH 2. Again, the issue that could be raised here is that neither graphene nor specific silanes are necessarily very cheap; there is thus a need to further transfer these reactions and concepts to cheaper and more readily available carbon materials.

In a somewhat different approach, Bashir et al.[158] used carbon materials produced from sugarcane bagasse to directly bind heavy metals (Cd and Cr) in contaminated soil to prevent (or at least reduce) uptake of the heavy metals by crops and to improve microbial activity favoring plant growth. Biochar

was produced via a rather simple process using pyrolysis at 500 °C for 2 hours. As the raw materials have a particles size in the millimeter range, the resulting products are rather coarse grained. The authors demonstrated that the application of the resulting biochar reduces the concentrations of free Cr and Cd by up to 85%. In particular, experiments in real soil samples demonstrated a high effectivity even at comparably low doses of added carbon to the soil of 15 g/kg of soil. The authors did follow this up and also measured the heavy metal uptake in plants grown on treated soils and found a significant decrease in Cd and Cr content in the respective plants. Moreover, biochar addition also positively affects the microbial activity. Overall this is therefore a highly interesting approach towards removing heavy metals not only from open surface waters but also in food production.

Finally, Saranaya et al.[159] used *Annona reticulata* Linn fruit peels to remove Cr(VI) from aqueous solution. The somewhat unique aspect of this study is the fact that the authors do not seem to have heat-treated or carbonized the materials. Rather they appear to have used the oven dried materials directly for the adsorption experiments. This is an interesting aspect because it reduces the energy and equipment cost involved in material preparation. Questions that need to be addressed, however, involve the long term stability of such a materials upon exposure to aqueous media. The authors highlight that their materials is among the best performing fruit peel-based adsorbent for Cr(VI) reported so far with a maximum capacity of 111 mg/g.

Overall, biomass and biomass derived materials are clearly a benchmark technology in low cost-high performance approaches for Cr removal from water and aqueous media. There are however, alternative approaches that will be discussed next.

Composites

Besides carbon, composites are of interest because they can combine the advantageous properties of carbon or organic matter such as open pore structures and high surface areas with advantages of inorganics such as high sorption capacities or high mechanical stability. Indeed numerous composites have been reported for Cr removal from water [133, 147].

Xu et al.[160] have prepared magnetic carbon/magnetite nanocomposites with high surface areas, Figure 6. The synthesis of the materials was achieved by electrospinning of polystyrene in a fibrous mesh followed by calcination in the presence of ferric nitrate producing robust magnetic carbon composites. The main feature of these materials is their capability to adsorb Cr(VI) as CrO_4^- very rapidly. The authors report high adsorption rate constants up to $1.64 \text{ mg/g}\cdot\text{min}$.

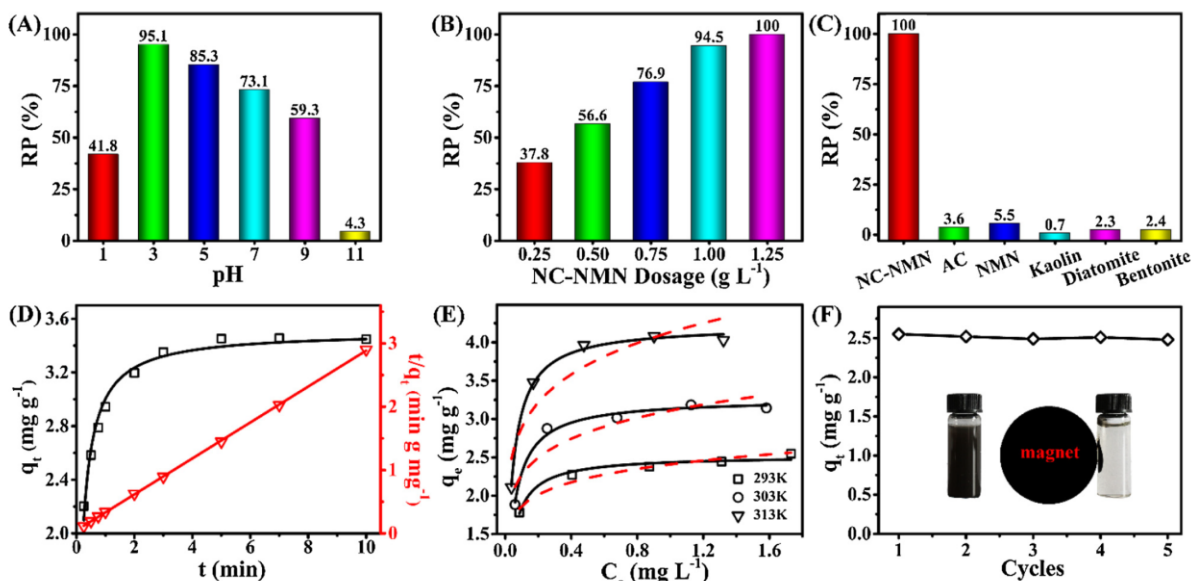


Figure 6. (A) Removal percentage (RP%) of Cr(VI) vs. pH, (B) effect of different adsorbent dosages, (C) comparison of Cr(VI) adsorption performance, (D) Cr(VI) adsorption rate q_t vs. t for and corresponding kinetic plot, (E) Cr(VI) adsorption isotherm at different temperatures, (F) Cr(VI) adsorption retention on magnetic carbon composite. Figure and caption reprinted from ref. [160] with permission.

Kumar et al.[161] developed a similar system. The combination of graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) with magnetite nanoparticles provides a new material that adsorbs heavy metals, in particular Cr(VI), and at the same time also reduces organic compounds such as p-nitroaniline using a photocatalytic process. The authors report a very high adsorption capacity of 555 mg/g for Cr(VI). This value is assigned to the presence of numerous $-\text{OH}$, $-\text{NH}_2$, $-\text{NHR}$, and other coordinating groups. Interestingly, the surface areas of these materials are below $100 \text{ m}^2/\text{g}$. The materials show an excellent

Cr(VI) and Cr(III) removal efficiency approaching 99% at higher pH. This is an interesting difference to carbon-based materials such as those discussed above[153-159], which show high adsorption capacities at low pH but perform rather poorly at high pH.

Xing et al.[162] synthesized iron oxide nanoparticles with an aminosilane surface coating. The combination of amino groups and nanoscale dimension of the material leads to rapid Cr(VI) removal kinetics such that solutions containing up to 100 mg/L were Cr-free within one minute. Moreover, the materials can easily be recycled by a simple washing process. On the other hand the Cr adsorption capacity is rather low at 8 mg/g.

Greenstein et al.[163] have developed iron oxide/polymer composites, including core-shell nanofibers for heavy metal removal. To produce the composite filter materials, the authors used electrospun poly(acrylonitrile) (PAN) fiber mats with embedded iron oxide nanoparticles to generate PAN/hematite composites with different iron oxide loadings. The resulting fiber mats Figure 7, remove As(V), Cr(VI), Cu(II) and Pb(II) and “generally matched expectations from more traditional iron oxide sorbents“. The article highlights two interesting aspects that extend beyond more classical adsorbents: (1) core-shell hybrid fibers prepared by the authors show a significantly higher performance and (2) the materials, being filters as they are, are able to remove suspended solids along with dissolved metal ions. This is certainly an interesting combination of capabilities with tremendous application potential.

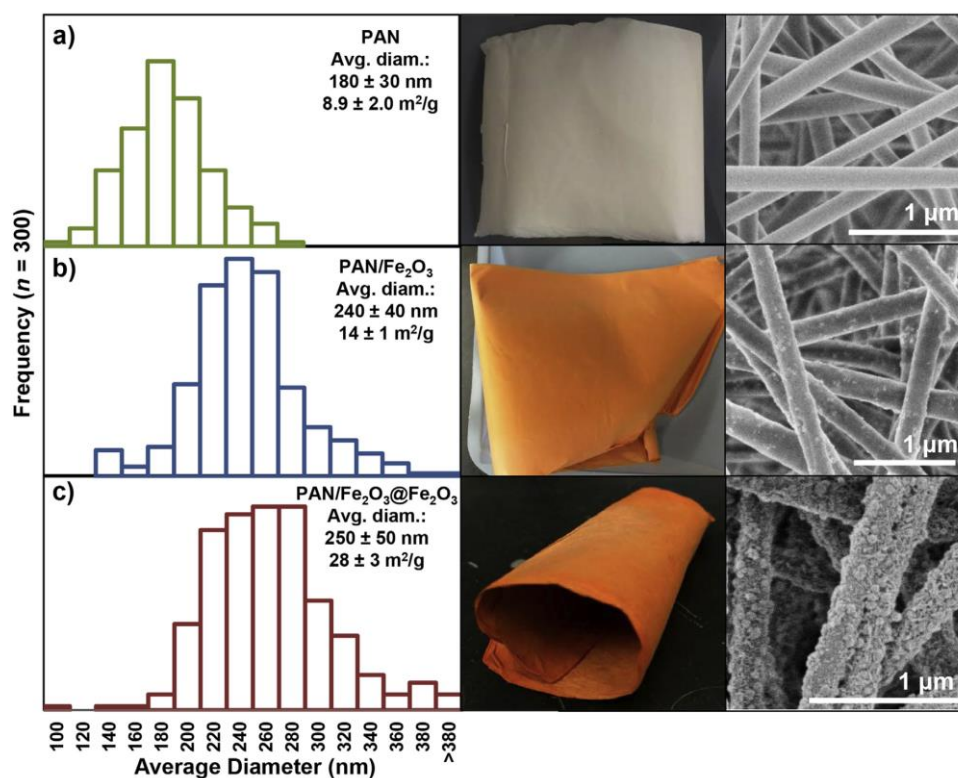


Figure 7. Size distribution histograms, photograph of the fiber mat, and SEM image of the fiber mats for (a) PAN, (b) embedded PAN/Fe₂O₃, and (c) core-shell PAN/Fe₂O₃@Fe₂O₃ nanofibers. Figure reprinted from ref. [163] with permission.

Finally and using a different approach, Sathvika et al.[164] used *saccharomyces cerevisiae* and *rhizobium* in combination with carbon nanotubes to remove Cr(VI) from aqueous solution. The cell wall of the biological species are held responsible for the effective adsorption of the Cr(VI) ions to the materials. As the authors highlight in their article, the work illustrates the “confluence of biotechnology and nanomaterials as an emerging area towards heavy metal remediation“.

Inorganics

A further extension of adsorbent materials is the use of fully inorganic adsorbents. Again, these studies have been reviewed [147, 150] but a few new developments should be highlighted. Hajji et al.[165] studied the adsorption of chromate onto siderite, ferrihydrite and goethite. The focus of this study is not on the optimization of adsorption capacities or adsorption rates. Rather the authors

performed an in-depth analysis of the (competitive) adsorption of Cr(VI) and related species. The data provide clear evidence that the material (adsorbent) architecture is a key parameter to control for adjusting not only adsorption but also desorption behavior.

Similarly, Wang et al.[166] studied the role of calcium polysulfide (CPS) in CPS/iron oxide composite materials, Figure 8. Again, the study focuses on the role of the iron species and the polysulfide in these adsorbents and the authors propose that an electron shuttling processes between all constituents is responsible for effective Cr(VI) adsorption along with reduction of Cr(VI) to Cr(III). The sulfur species and the redox couple Fe(II)/Fe(III) are assigned key roles in this process. This is an interesting and detailed account of how adsorption and redox chemistry combined could provide new approaches to water treatment.

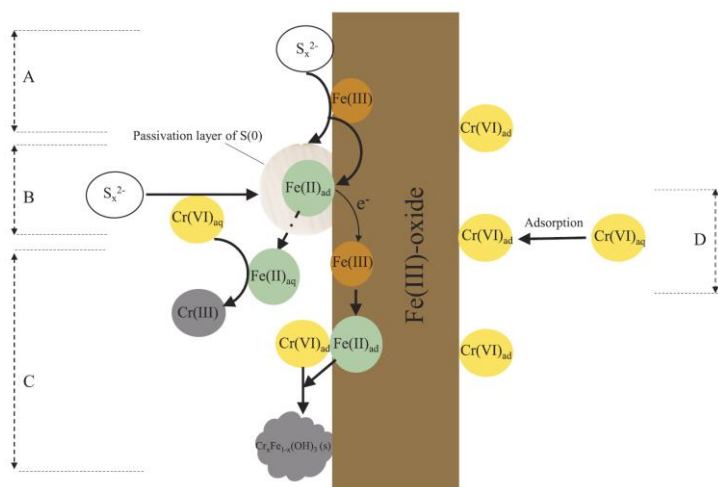


Figure 8. Proposed mechanism of iron oxide-promoted Cr(VI) sequestration using CPS under acidic conditions. Reprinted from ref.[166] with permission.

Wang et al.[167] report on the use of sulfidated zerovalent iron for Cr(VI) and Sb(III) removal. Similar to the previous study[166] these authors report a clear influence of the sulfur present in the adsorbents on performance of the materials. Especially the Fe/S ratio controls the efficiency of Cr(VI)

and Sb(III) removal and the presence of Sb(III) promotes Cr(VI) removal, while the inverse effect was not observed.

Whitaker et al.[168] explored the use of biogenic iron oxides (BIOS) for Cr(VI) uptake. The rationale behind this approach is that BIOS are nanocrystalline, have a high surface area, and are often partly porous. Moreover, they contain many defects in their crystal structure to accommodate foreign ions like Cr(VI) and they often also contain organic components that may further enhance the adsorption capacities and/or the adsorption rates. Similar to ref.[166], Whitaker et al.[168] do not focus on improving adsorption behavior. Rather they focus on understanding the mechanisms and single processes that happen during adsorption and Cr(VI) reduction to Cr(III). They again propose an electron transfer from Fe(II) to Cr(VI), again similar to ref.[166] but through a less complicated pathway.

Suzuki et al.[169] follow similar ideas but using fungal Mn-oxides (BMOS) rather than BIOS. In contrast to all studies discussed so far, this work focuses on Cr(III) and the authors show that BMOS are effective oxidizers for Cr(III) to Cr(VI) under aerobic conditions. Moreover, BMOS are effective adsorbents for Cr(III) reaching a maximum of ca. 120% of Cr(III) with respect to the molar Mn content. While the oxidation and release of Cr(VI) is an issue, the very high Cr binding capacity of these materials is clearly an asset.

Finally, Thomas et al.[170] have studied a series of green rusts for Cr(VI) remediation. The particular focus of their study was the investigation of cation substitution within the green rusts and the effect on Cr uptake. The most obvious effect was that Mg(II) effectively stabilizes the green rust and thus provides a solution to a common problem with green rust, namely the low stability if exposed to environmental conditions. The authors suggest that Mg-stabilized green rusts could be a viable adsorbent for Cr(VI) remediation and, moreover, that these materials could also be sinks for bivalent metal ions such as Ni(II) or Cu(II).

Gels and Resins

While there are numerous organic adsorbents that have been published[147] including algae,[148] gels and resins have attracted attention as well. To just highlight a few recent approaches, Zhang et al.[171] used Fe-crosslinked alginate hydrogels to perform a synergistic redox reaction between Cr(VI) and As(III) resulting in Cr(III) and As(V), both of which can then be removed to over 80% from aqueous solutions using the as-prepared hydrogels. The key responsible functional component is the Fe(II) ion, which forms upon irradiation and enables the reduction of Cr(VI) to Cr(III) to start the reaction cascade.

Kou et al.[172] used recombinant proteins to produce protein hydrogels containing specific metal or oxoanion binding domains, e.g. to bind chromate. While the synthesis is rather complex, the power of the approach lies in the fact that protein binding motifs can be combined to even address complex situations containing numerous heavy metal species at the same time.

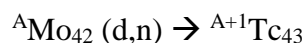
Xie et al.[173] used hyper-crosslinked polymeric ionic liquids to remove Cr(VI) in highly competitive conditions with Cl^- , NO_3^- , H_2PO_4^- and SO_4^{2-} present in the solution. The crosslinked resin can be recycled and – exploiting an advantage that is intrinsic to all ionic liquids – can be adjusted to account for changes in the application by exchange of ions.

Finally, Hesemann and coworkers have used ionosilicas to remove chromate from aqueous solution [174]. The high number of positive charges in these materials provides solid adsorbents with high capacities of up to 2.6 mmol/g.

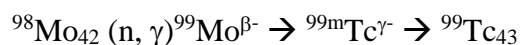
11.4.3 Pertchnetate as an example of a radioactive oxoanion

Technetium is an element, which presents in aqueous solution many oxidation degrees, from +VII to -I [175]. The most stable oxidation state in aerated solution is +VII, in the form of the oxoanion TcO_4^- . The redox chemistry of this element is very complex and several disproportionation reaction result in the co-existence of several oxidation states in equilibrium in solution [175]. The chemical forms are very different with coordination numbers between 4 and 9, and come in the form of oxoanion, cation, oxocation and neutral species with low solubility, such as TcO_2 , or volatile as

Tc₂O₇ or the salt of CsTcO₄ [176]. While this chapter focuses on the oxoanion TcO₄⁻, it is important to notice that several reservoirs at different oxidation states are likely to exist in the environment. Technetium is a radioelement, meaning that all isotopes (from 90 to 110) are radioactive [177]. The toxicity of this element is therefore both chemical (that of a heavy metal) and radiochemical (radiotoxicity). Technetium is a natural, non-primordial element formed by spontaneous fission of the uranium isotope 238. The quantities in the earth's crust are very small below $\ll 10^{-15}$ mol.L⁻¹ [178]. This element on earth is mostly anthropological. It was first produced (^{95m}Tc₄₃ and ^{97m}Tc₄₃) by man using a cyclotron at the University of Berkeley by Lawrence, following the irradiation of a natural molybdenum target by deuterons, according to the nuclear reaction:



Synthesis by artificial means led to its name, which means "artificial" in Greek. It has been isolated is characterized first by Perrier and Segré in 1937 [175]. The use of techniques of trace chemistry developed in radiochemistry and the analogy with the other elements of group VII (with Mn and Re) of Mendeleïev's periodic classification made it possible to describe initially its chemical properties of this [177]. Only three isotopes have a radioactive decay period longer than 61 days. These are the isotopes 97, 98 and 99 with a half-life greater than 10⁵ y (97 - T_{1/2} = 2.6 10⁶ y, 98 - T_{1/2} = 4.2 10⁶ y and 99 - T_{1/2} = 2.13 10⁵ y) [175]. As these isotopes are radioactive, they must be handled in facilities dedicated to the handling of radioactive substances [179]. The one present in the largest quantity is the isotope ⁹⁹Tc, which is a soft beta emitter (E_{max} = 0.29 MeV), with no associated gamma radiation emission. The specific activity is 6.36 10⁸ Bq.g⁻¹. It is mainly produced by the fission reaction of fissile isotopes such as ²³⁵U or ²³⁹Pu. The quantity depends on the nuclear reaction, the fuel (²³⁵U, ²³⁸U, ²³⁹Pu, ...) and the burnup. For example, there is about 1 kg of Tc per 1 ton of uranium in spent nuclear fuel [180]. The best-known isotope, especially for medical applications, is the metastable ^{99m}Tc isotope (radiopharmaceuticals isotope). It is mainly produced by irradiation of ⁹⁹Mo by neutrons according to the following nuclear reactions:



The half-life of ^{99}Mo is $T_{1/2} = 2.75$ d. The transition from $^{99\text{m}}\text{Tc}$ to ^{99}Tc leads to the emission of gamma radiation of the order of 140 keV with a very short half-life of $T_{1/2} = 6.02$ h [175].

Technetium is present in the environment mainly due to the human activities [181]. There are two particular areas: nuclear testing and preparation of plutonium for these weapons, and nuclear reactor accidents. Concerning atmospheric testing of nuclear weapons, it should be noted that the fission of the ^{235}U and ^{239}Pu nuclei produces ^{99}Tc , in a volatile form of Tc(VII) (Tc_2O_7) at high temperature. Hydrolysis in the atmosphere leads to the formation of the anion TcO_4^- . Concerning the production of plutonium for military applications, the joint production of Tc and its subsequent separation with other fission products leads to the accumulation of a very large amount of Tc, a fraction of which is released into the environment from the fission product storage vessels. The release of ^{99}Tc during the accident at the Chernobyl (Ukraine) reactor in 1986 and Fukushima (Japan) reactor in 2011 also led to the release of the TcO_4^- anion into the atmosphere from volatile Tc(VII) species (Tc_2O_7 and CsTcO_4 , mostly). The amount of artificial Tc present in the environment has been estimated to be in the order of 2 tons ($1.3 \cdot 10^3$ TBq) and the chemical form in aqueous media under aerobic conditions is indeed Tc(VII) in the form of the TcO_4^- anion [178].

It is in the spent fuel cycle of nuclear power that the quantity of technetium (^{99}Tc) accumulated is the highest [182]. During the reprocessing, the release into the environment is controlled. Depending on whether the spent fuel cycle is closed (as in France, Japan, ...) or open (as in the United States, ...), the Tc is present either in a dedicated containment matrix or in the fuel. The chemical form is multiple, ranging from zero oxidation state (Tc metal) to a pertechnetate salt, via TcO_2 . Regardless of the conditioning (containment matrix or spent fuel), this nuclear waste will be stored in suitable geological disposal sites. However, it should be noted that the transmutation of ^{99}Tc by nuclear reactions (neutron) leads to stable Rh and Pd nuclides. Concerning the use of the $^{99\text{m}}\text{Tc}$ isotope in medical applications, the quantity involved is very small but will most likely increase with the

development of nuclear medicine in the world [183]. For medical applications, the chemical form is also extremely variable. The most common forms are the TcO_4^- anion and complexes in solution of the oxidation state +V and +III, like TcO^{3+} and Tc^{3+} cations, To conclude, the speciation of the Tc element in environmental aqueous media generally depends on aerobic or non-aerobic conditions. In an aerobic environment, Tc will mainly be in the oxidation state +VII, in the anionic form TcO_4^- , whereas in an anaerobic environment, Tc can exist in different oxidation states: the oxidised form Tc(VII), therefore TcO_4^- , and the reduced form Tc(IV), TcO_2 [184, 185]. This will also be linked to the presence of redox agents in the environment and the presence of complexing agents such as carbonate anions, humic acids or chloride ions depending on the geological site [175, 176]. Given the low concentration of Tc, radioactivity (the specific activity of ^{99}Tc is 6.36 Bq.g^{-1}) is generally used as a unit of mass (Bq.g^{-1}) and volume (Bq.L^{-1}) concentration.

The pertechnetate anion in aqueous solution, often after a redox reaction, has a strong capacity to sorb onto mineral surfaces (rocks, sediment and soils) and to accumulate in plants and microorganisms [178]. These natural compartments therefore constitute an important reservoir of the element Tc in the environment and it is important to consider them for the remediation of aquatic environments. The concentration of ^{99}Tc in aquatic environments is highly variable (several orders of magnitude), and greatly depends on the location of the sampling: near or far from a source of Tc. It also depends on the date of the measurement: before or after nuclear test shutdowns, accidents at the Chernobyl and Fukushima reactors or the reduction of Tc release in spent nuclear fuel processing operations. The orders of magnitude range from 0.02 Bq.L^{-1} to 20 Bq.L^{-1} (close to Monaco in 1986, May) [186] in rainwater, and from $10^{-5} \text{ Bq.L}^{-1}$ to $10^{-1} \text{ Bq.L}^{-1}$ in seas and oceans [181]. These concentrations are well below $10^{-10} \text{ mol.L}^{-1}$, which is extremely low on the chemical scale. The concepts of radiochemistry (trace scale chemistry) are generally used to describe the speciation of ions in solution [187]. Even though these concentrations are very low, the radiotoxicity of ^{99}Tc is very high and the long-term risk associated with humans is very significant.

Very few studies concern the remediation of natural waters (groundwater, rainwater, lakes, rivers and seas and oceans) by technetium. The vast majority of the work concerns the treatment of industrial solutions resulting from the production of plutonium for military applications [188] and to a lesser extent the management of waste from medical applications [89, 189]. However, it should be noted that there is vast literature concerning either the separation of technetium in PUREX separation processes (separation of uranium and plutonium from fission products such as ^{99}Tc), or the remediation of storage tanks for fission products from the preparation of "military plutonium". In these processes, liquid/liquid extraction and separation on ion exchange resin are often used. In the case of separation by liquid/liquid extraction, ammonium extracts or molecular or supramolecular complexing agents are commonly used [190].

While liquid-liquid extraction techniques are very well suited for the separation of constituents in macro concentration, this technique is poorly suited for species that are very diluted in the environment, such as pollutants, which require extremely large volumes of solutions. Moreover, in the case of radioactive pollutants, the subsequent management of organic solvent or ion exchange resins contaminated with a radioactive substance is an additional constraint. This work will not be further developed here but is routinely presented at the annual specific Tc and Re chemistry conference (ISTR - International Symposium on Technetium and Rhenium - Science and Utilization). These more conventional approaches are not developed in this chapter, but many publications are available in the literature [16, 188-194]. However, recent developments concerning the use of bi-functionalized anion exchange resins for the recovery of TcO_4^- from groundwater should be noted [195].

Furthermore, in the case of the separation of a radioactive element, it is necessary to consider the effect of ionising radiation on the separation system. For example, mineral supports are often preferred over organic supports due to the radiolytic degradation of the more fragile organic bonds [196]. Finally, it should be considered that selectivity is extremely important for trace elements because other contaminants in the environment, which are not always radioactive, may be present at

much higher concentrations (10^3 to 10^6 times higher). Moreover, it is also important to consider the management of the radioactive waste after separation. In the most recent work, the separative system developed is also intended to be transformed into a containment matrix [88, 197, 198]. In addition, it should be noted that the constraints linked to the handling of a radioelement such as Tc often lead to the use of stable chemical analogues such as ReO_4^- and ClO_4^- or the $^{99\text{m}}\text{Tc}$ isotope in the ultra-trace state, which is easy to detect thanks to its gamma emission.

The most recent scientific approaches developed for the separation of Tc are globally of two types: separation by ion exchange on Metal-Organic Framework (MOF) supports and adsorption on active surfaces of nanoparticles. Other more innovative systems will not be discussed here, such as organic adsorbents (layered double hydroxide) or dendrimer systems [16, 199].

Recent work shows the practical interest and promise of MOF materials for the treatment of solutions contaminated with radioactive anions such as $^{129}\text{I}^-$, $^{79}\text{SeO}_3^{2-}$, $^{79}\text{SeO}_4^{2-}$ and $^{99}\text{TcO}_4^-$ [190, 200]. These cationic MOFs are built from neutral soft donor ligand and transition metal. A few main criteria seem to guide the synthesis of MOFs in order to amplify the interaction with the TcO_4^- anion: i) the exchange anion used for the construction of the MOF must be compatible with the medium and must constitute pores/channels suitable for anion exchange (ClO_4^- , Cl^- , NO_3^- and SO_4^{2-}), ii) the hydrophobic nature of the surface of the material and of the pores/channels is an asset for selectivity and iii) the possibility of creating a network of hydrogen bonds.

The choice of transition metal is also important. For the capture of the TcO_4^- anion, two MOF structures have been specifically studied: SCU-100 and cationic Zr-based MOF [200, 201]. Recently, an 8-fold interpenetrated three-dimensional cationic MOF material SCU-100 has shown high immobilization capabilities for TcO_4^- anion with fast kinetics. Sorption isotherms were measured at room temperature with TcO_4^- or ReO_4^- . The good selectivity towards other anions, which are present in higher concentrations than Tc, and the radiostability of the structure are further evidence of the interest of these new materials. The proposed mechanism is based on anion exchange and strong

interaction between the Ag^+ sites constituting MOF SCU-100 with the tetradentate neutral nitrogen-donor ligand. The single crystal X-ray diffraction on the ReO_4^- -based structure highlights the coordination between the two metals, Re and Ag (Re-O-Ag), and the existence of several hydrogen bonds.

Hesemann and coworkers have developed a strategy using a platform made from mesoporous silica [202]. Indeed, it is possible to covalently bind reactive chemical functions. These properties have been exploited by using an imidazolium unit and different alkyl chain lengths between the mesoporous network and the imidazolium cation, and also the one fixed on the second nitrogen of the imidazolium. These ion exchangers show a very good extraction capacity of the TcO_4^- anion and especially an excellent selectivity against other anions, Figure 9. These results were explained by the hydrophobicity of both the mesoporous silica support and the presence of alkyl chains. The alkyl chains also allow the structuring of the mesoporous silica/water interface by a network of hydrogen bonds.

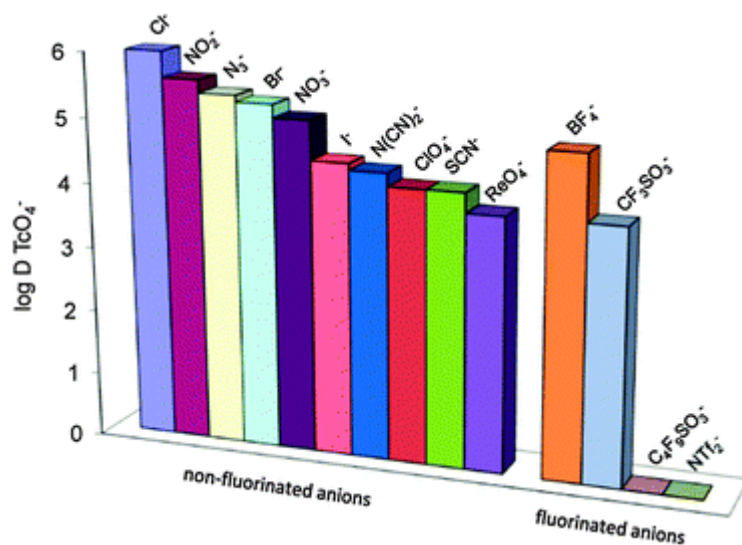


Figure 9. Distribution coefficients of TcO_4^- in the presence of different competing ions ($c = 0.1 \text{ mol L}^{-1}$). Reprinted from [202] with permission.

Shen et al.[203] studied technetium removal from water. The separation is based on the sorption of the anion ReO_4^- (as TcO_4^- surrogate) on an ordered urea-functionalized mesoporous polymeric nanoparticle (urea-MPN). The nanosized spherical morphology and 3D interconnected ordered cubic mesopore structure was obtained by the surfactant directed self-assembly process with the low-concentration urea-phenol-formaldehyde resol oligomers under hydrothermal conditions. The sorption capacities of this material are good with fast kinetics (less than 30 minutes). Analysis by NMR and XPS spectroscopies showed that the mechanism involves the effective hydrogen-bond provided by the urea functional groups bonding the tetrahedral anion ReO_4^- . In addition, the nanometric dimensions of the channels and the large specific surface favours the diffusion of the anion. Finally, the hydrophobic pore surfaces of the urea-MPN are also beneficial for decreasing the ReO_4^- charge. Selectivity towards other anions such as nitrate, carbonate, phosphate and sulfate ions. The stability of the ordered mesoporous structure is maintained after an irradiation with 200 kGy dose radiation.

In a recent study [204], the recovery of the ReO_4^- anion (used as a simulant of TcO_4^-) from nanoparticle-anchored biochar composite (ZBC) ZnO was observed. In this study, selectivity towards competitive anions (such as I^- , NO_2^- , NO_3^- , SO_4^{2-} , PO_4^{3-} , ...) and stability towards gamma radiolysis were evaluated, and are very favorable. It has been shown that the high sorption capacity of the ReO_4^- anion is due to the synergistic effect of the hydrophobicity (superhydrophobicity) of the surface and the nature of the sorbent (and in particular according to the different crystal planes of the ZnO nanoparticles). The electron transfer between ReO_4^- and the (002) surface of ZnO appears to be greater than with the (100) plane, leading to a stronger interaction for the (002) plane.

11.4.4 Diclofenac as an example of an organic anion

Due to the huge anthropogenic activities (pharmaceutical industry, agriculture), pollution is not limited on purely inorganic species, but organic ionic species also have a strong ecological impact

on various natural compartments. The incorporation of ionic groups is a common strategy to modify the physical properties of organic compounds and consequently, numerous organic compounds exist as ionic species. This is due to the fact that water solubility is often required for an efficient use of organic compounds as pesticide, pharmaceutical drug or dye. Indeed, various types of organic anions such as anionic pharmaceuticals and anionic dyes are extensively used in different industries and some of them are produced on a large ton-scale [8, 205, 206].

These organic anions display interesting properties such as biological activity, useful optical properties, etc. This renders them interesting for various applications in medicine, agriculture, catalysis, sensors, solar cells, printing, textiles, bioimaging and energetic materials. Various pharmaceutically active compounds (PhACs) and, more generally, Pharmaceutical and Personal Care Products (PPCPs) [207] are organic and ionic. The presence of organic anions in water bodies is therefore closely related to anthropogenic activities, and these compounds are widely spread all over the planet. The high water solubility of these compounds, which is often a key property for the use of these compounds as pharmaceutical or pesticide, further increases their mobility in natural compartments, in particular in soil and water bodies. The water solubility therefore favors rapid distribution of these compounds and hampers their elimination via water treatment processes.

Synthetic anionic organic species have been present in the environment since decades, but only recently, significant progress in analytical methods (such as GC-MS and LC-MS) allowed for a detailed monitoring of these compounds. This is particularly true for water bodies where these compounds can exist in concentrations down to the ng/L scale. These studies clearly show the omnipresence of a wide range of pharmaceuticals and pesticides. The data also indicate a continuous influx of these compounds into the biosphere. Anionic organic compounds are therefore ubiquitous and particularly abundant in surface, ground and drinking water. They can also be found in other environmental compartments (soils) and, due to the water treatment and upgrading processes, also in sewage sludge and even the effluents of WWTPs. The presence of these compounds in the environment can cause direct and indirect harm to humans, animals and plants. Besides the purely

inorganic oxoanions such as chromate, nitrate etc., organic anionic species therefore have a tremendous impact on water management aspects. Their monitoring, separation and removal from diverse water bodies and particularly from wastewater is therefore a significant challenge and of essential concern for human health.

Pharmaceuticals are an important class of emerging contaminants [208]. This is (1) due to their inherent biological activity and (2) because these compounds typically enter the aquatic environment after application. One compound in particular, (2-[2,6-dichlorophenylamino]phenylethanoic acid) (Diclofenac, DCF), is among the most prominent examples of such a species. Even though DCF is not an oxoanion but a classical organic anion, we chose to discuss its dissemination and monitoring in this chapter. Indeed, DCF is among the most studied and most often detected pharmaceuticals worldwide [209], and huge data indicating DCF pollution is available. DCF is an excellent model compound allowing monitoring the challenges related to the management of anionic organic species and their metabolites in water treatment and upgrading. It represents a large panel of organic carboxylates, sulfonates, phosphonates, etc. which are widely used as water soluble drugs, dyes and pesticides and which are present in nearly all natural compartments.

Due to its intensive use both in human medicine and for veterinary applications, DCF is detected in nearly all water bodies (wastewater, surface water, effluents). It was therefore included in the EU watch list of pharmaceuticals requiring detailed environmental monitoring in 2014 (Directive 2014/80 of the EU) [92] but has recently been removed from that list as sufficiently monitoring data are now available. Today, DCF is omnipresent in nearly all natural compartments (aquatic environment, soil). This part gives a short overview about the use of DCF, its fate in different natural compartments and the consequences and repercussions of its presence in these ecologic systems (Figure 10). The fate, effects and risks related to the presence of DCF in the environment have recently been reviewed by Sathishkumar et.al.[9].

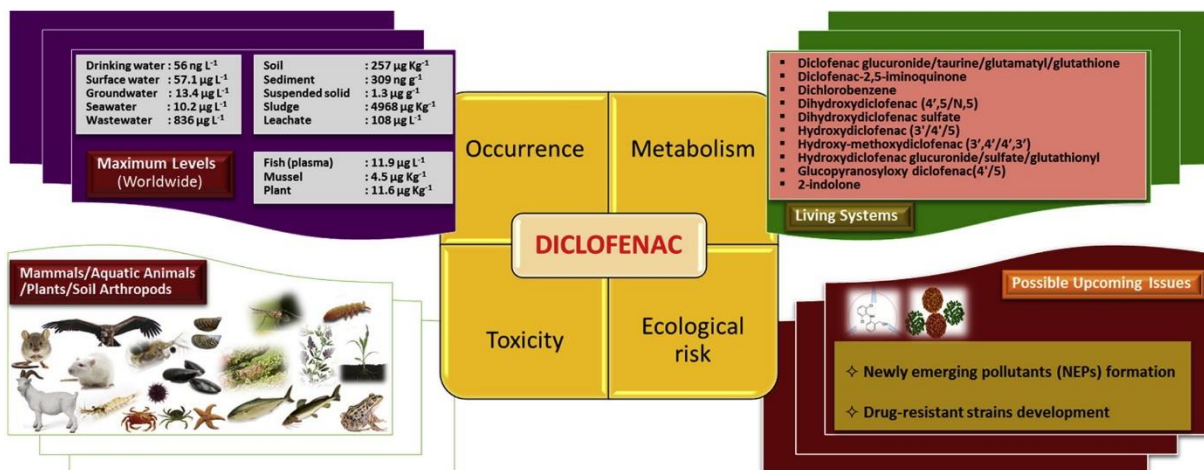


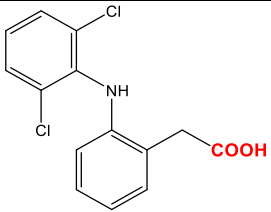
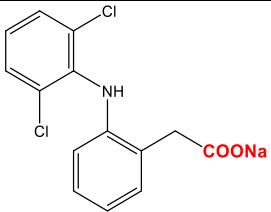
Figure 10. Diclofenac: metabolism, occurrence in the natural environment and ecological risk on human and animal health. Reprinted with permission from ref.[9]

DCF is a nonsteroidal anti-inflammatory drug (NSAID), similar to other widely used pharmaceuticals such as Ibuprofen, Naxopren, Ketoprofene and Aspirine. NSAIDs are ‘over-the-counter’ drugs in most countries. These drugs are easily accessible and therefore used both in human medicine and for veterinary purposes. Nowadays, DCF is one of the most frequently administered agents for pain relief and inflammatory diseases in humans and animals.

DCF was introduced in the 1960s by Ciba-Geigy [210]. Today, DCF is commercialized under different brand names (Athrifen, Diclodoc, Diclofenbeta, Voltaren and many others). It is usually commercialized as sodium or potassium salt and is applied *via* oral or topical administration. Some physical properties of diclofenac (free acid) and diclofenac-sodium salt are summarized in Table 2.

Table 2. Comparison of some physical and chemical properties of diclofenac and diclofenac-sodium

	Diclofenac - free acid	Diclofenac-sodium

Structure		
Formula	$C_{14}H_{11}Cl_2NO_2$	$C_{14}H_{10}Cl_2NNaO_2$
Molecular weight	296.15g/mol	318.13 g/mol
CAS number	15307-86-5	15307-79-6
Water solubility	2.43 mg/L [211]	20.4 g/L [212]
Melting point	158-159°C	283-285°C

Although DCF is widely used, there is a lack of reliable data about its annual production and consumption. The estimated global annual consumption was ca. 940 tons in the early 2000s and approx. 1500 tons ten years later [213]. However, these values only concern human health applications and neglect veterinary use. This difference is important due to intensive veterinary use of DCF and particularly to the different fate of drugs used for human and animal diseases. Whereas drugs used for human health applications mostly enter the water treatment circuit *via* WWTPs, drugs originating from veterinary uses mostly move directly into the aquatic ecosystem, *i.e.*, in surface water, without further treatment.

As DCF is a low-cost over-the-counter drug, it is extensively used both in emerging and developed countries. This is highlighted on the one side by the estimated data for Brazil and the Indian subcontinent with annual consumptions of more than 60 tons in each country and its estimated consumption in Germany (82 t in 1999), France (16 t in 2003) and England (26 tons in 2000) [213]. Unfortunately, no precise recent data exist. In spite of this, the available data clearly indicate that DCF is a widely used and globally present drug. It is therefore a valuable model compound to monitor the spread and fate and to evaluate the effects of the presence of anionic organic species and in particular of pharmaceuticals in the ecosystem.

The presence of DCF in the environment sometimes has serious consequences. First studies indicating deep impact of DCF on the environment go back to the early 2000s. DCF was held responsible for a sharp decline in the population of three vulture species in the Indian subcontinent due to the consumption of carcasses of cattle treated with DCF. The intolerance of these birds toward DCF leads to renal failure and finally to their death [98]. A similar scenario led to the breakdown of other vulture and eagle populations in Kenya ten years later [214]. To prevent further decline in vulture population, the use of DCF for veterinary use has therefore been banned in India, Nepal and Pakistan since 2006.

The fate of DCF is of significant concern and was thoroughly studied. Detailed data on the human, animal and plant metabolism of DCF exist (Figure 11). They reveal the presence of its metabolites in various environmental compartments [8, 9, 17].

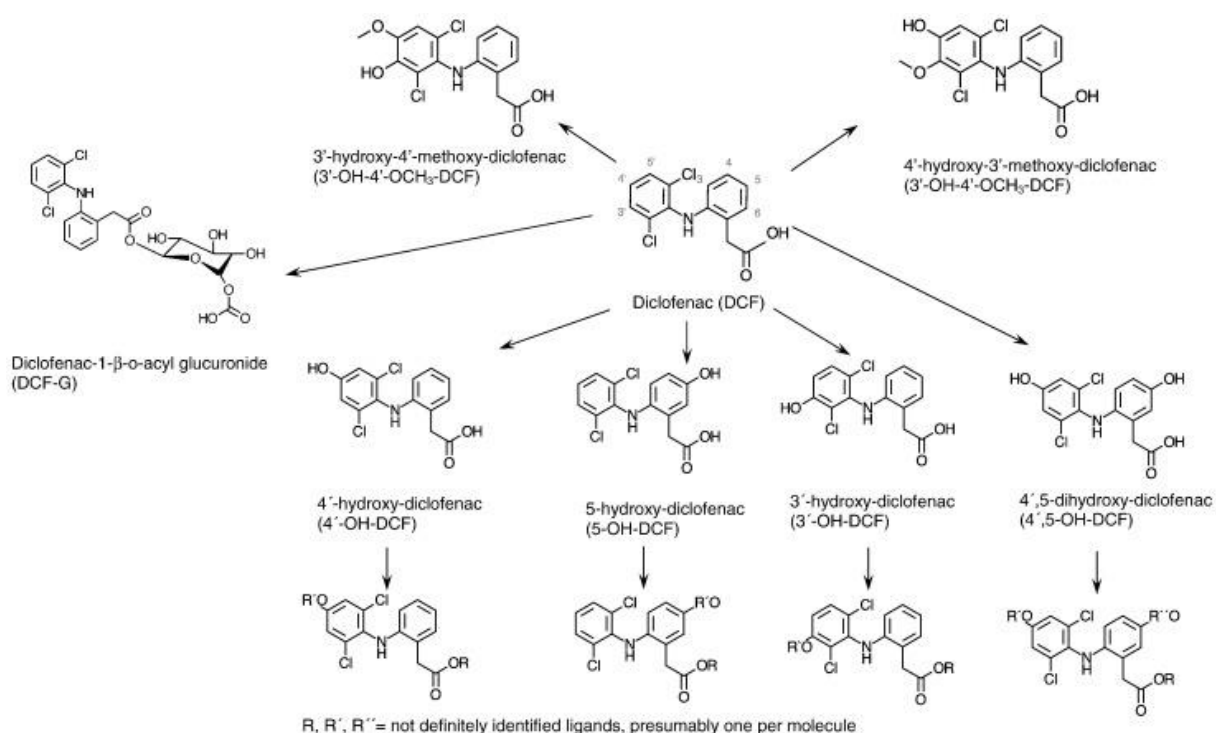


Figure 11. DCF and its main metabolites. Reprinted from ref.[215] with permission.

The human metabolism of DCF produces a variety of compounds, mainly hydroxylated DCF derivatives. The elimination half-life of DCF is 2 hours [216]. After this relatively short period, DCF is excreted either as such or as one of its metabolites, both via the urines (2/3) or the faeces (1/3) [17].

DCF is mainly metabolized *via* hydroxylation, with 4'-hydroxy (OH) diclofenac as major product [215], either as pure compounds or their conjugated forms with glucuronic acid, glucuronide, taurine or sulfate. DCF is nearly completely metabolized, only a minor part is excreted as the un-metabolized compound. Approx. 10% of the administered dose is eliminated as taurine, glucuronide or sulfate conjugates, and more than 80% as DCF derivatives, mostly hydroxylated species and their conjugates (Figure 12). Hence, the monitoring of DCF should not be limited on the pure drug, but must be extended to its metabolites.

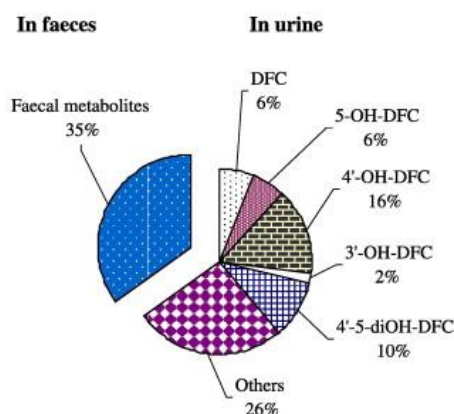


Figure 12. Identified metabolites of DCF and their percentages of oral dosage. Reprinted from ref.[17] with permission.

After excretion, DCF enters the aquatic environment, either directly or after its transit *via* wastewater treatment plants (WWTPs). The various entries of DCF and its metabolites are illustrated in Figure 13. DCF is initially introduced in surface water, but can later be found in ground water and even in drinking and mineral water, due to inefficient elimination during wastewater treatment. Due to the continuous influx of DCF and its metabolites into the natural environment, DCF is considered as a pseudo-persistent pollutant. Despite its relatively short half-life time in freshwater of 8 days [217], the pseudo-persistent nature of DCF makes in an important case study for organic anionic contaminants.

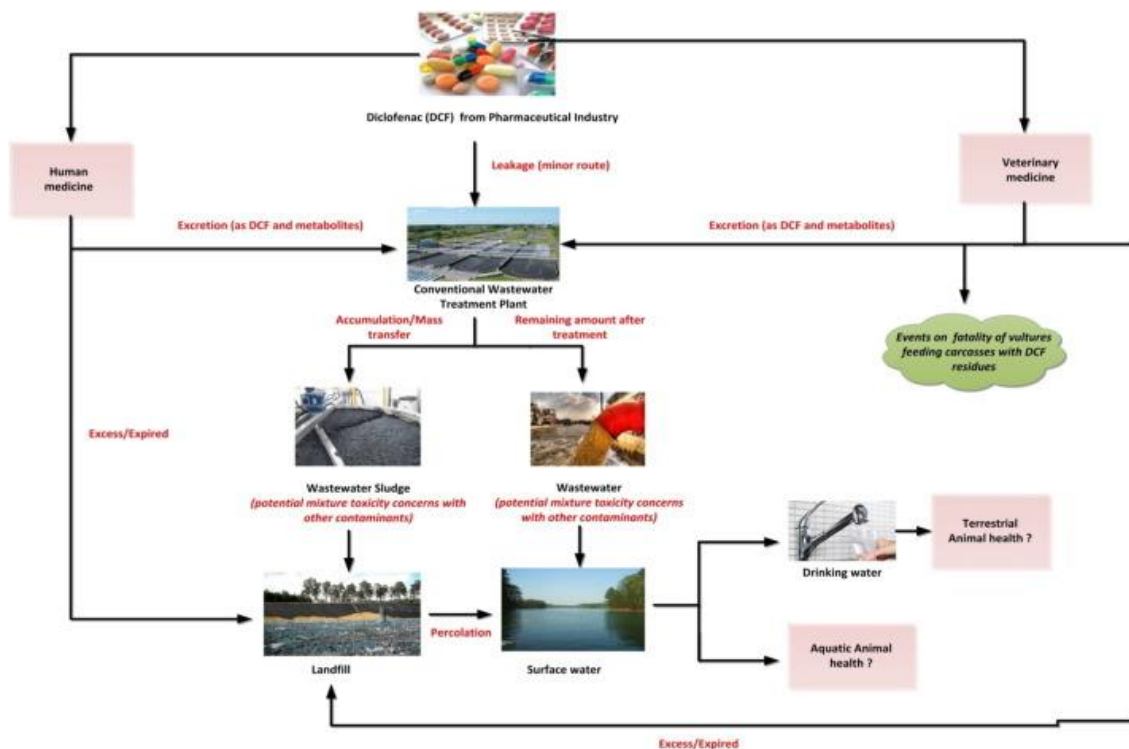


Figure 13. Entry routes of DCF into the environment. Reprinted from ref.[8] with permission.

We focus here on the monitoring of DCF in water bodies originating from France and Germany as representative examples of developed countries. The presence of DCF and its metabolites has been observed since the beginning of the 2000s. Selected data of DCF concentrations in surface, ground and wastewater together with some data from seawater are given in Table 2.

The first report on the presence of DCF in surface water appeared as early as 2002, when Heberer *et al.* reported a DCF concentration of approx. 1 µg/L in surface water in Berlin/Germany [218]. Since then, enormous amounts of data attest the omnipresence of DCF and its metabolites in almost all water bodies worldwide [9]. Remarkably, DCF was even found in surface water in very isolated regions such as the northern Antarctic Peninsula [219].

DCF residues could be found in nearly all types of *surface water* such as canals, lakes, rivers. The presence of DCF is clearly related to dense population or industrial or agricultural activities. It originates from pharmaceutical production sites, wastewater treatment plant effluents of urban and touristic areas or hospital effluents. [59, 220-223]. Both DCF and its metabolites were detected in surface water, in particular hydroxylated species and conjugate derivatives, resulting from human or

animal excretion. Some other derivatives such as nitro and nitroso derivatives could also be identified [224]. DCF and its metabolites were present in nearly all investigated samples in concentration in the range of 0.1 – 1 µg/L, but in some exceptional cases even in considerably higher concentrations of over 50 µg/L [225].

DCF has also been identified in *groundwater*, which is directly linked to its presence in surface water [226]. DCF in groundwater therefore originates from identical sources (agricultural, pharmaceutical, etc.) as in surface water. The presence of DCF residues in groundwater highlights its mobility in the soil. The pollution of groundwater is particularly problematic as these resources are often used for direct water supplies and for the production of drinking water. In general, the DCF concentrations in groundwater are slightly lower than those in surface water. This is probably due to a partial degradation of DCF by microorganisms in the soil. However, concentrations of 10 – 500 ng/L are usually observed (Table 3).

The presence of DCF residues in *drinking water* and especially *tap water* directly relates to human health issues and is therefore of particular importance. Despite water treatment, DCF has been found in different drinking water samples, including mineral water and tap water. The contamination of drinking water is widespread, as DCF has been found in samples in France and Germany (Table 3), but also in other countries (Sweden, Spain). DCF is generally present in traces with concentrations on the ng/L scale. The reason for the presence of DCF in drinking water is probably the inefficient elimination in WWTPs and inadequate treatment in Drinking Water Treatment plants (DWTPs), together with other reasons. It clearly appears that the pollution of drinking water with DCF and other pharmaceuticals is one of the challenges in water treatment in the near future and has to be followed in detail.

Besides surface, ground and drinking water, DCF residues are also found in other water bodies. As DCF is not efficiently degraded in WWTPs (*vide infra*), high DCF concentrations are also found in WWTP effluents and sewage sludge. DCF and several of its derivatives such as hydroxylated species or glucuronide and sulfate conjugates could be detected, originating from human or animal

excretion. The concentrations in surface water are generally in the range of several hundred ng/L up to several µg/L, in some exceptional cases even up to more than 50 µg/L.

Finally, the presence of DCF in the *marine environment* has recently been investigated [97]. Despite the relatively short half-life time of DCF in freshwater of approx. 8 days [217], DCF could also be found in various marine environments due to its continuous input from surface water. DCF is therefore particularly present in coastal waters and sediments although in lower concentration. However, the presence of traces of DCF has a serious impact on marine organisms due to the bioaccumulation of DCF. Mussels (*mytilus galloprovincialis*, *mytilus trossulus*) are particularly sensitive; this is due to their high filtration capacity and their ability to bioaccumulate pollutants [227]. The accumulation of DCF by mussels then generates oxidative stress and genotoxic effects [97]. DCF therefore seems to be responsible for various effects on marine organisms, including the alteration of biological functions.

Table 3. Selected data of DCF occurrence in various water bodies in France and Germany

Entry	Country	Sample nature	DCF conc.	sampling point	reference
1	France	Surface water	300 ng/L	Doubs river	[228]
2	France	Surface water	166 ng/L	Loue river	[228]
3	France	Surface water	33,2 ng/L	Lergue River	[229]
4	Germany	Surface water	435 ng/L	Lake Tegel	[230]
5	Germany	Surface water	245 ng/L	Saale River	[231]
6	Germany	Surface water	15.0 µg/L	Erft River (near Cologne)	[232]
7	Germany	Surface water	2.1 µg/L	Teltow canal (Berlin)	[233]
8	France	Groundwater	2.5 ng/L	Wells of Hérault basin	[229]

9	France	Groundwater	9.7 ng/L	Rhone-Alpes Region	[234]
10	Germany	Groundwater	590 ng/L	Monitoring wells	[235]
11	Germany	Groundwater	45 ng/L	Monitoring wells	[230]
12	France	Drinking water	56 ng/L	Rhone-Alpes water supply	[234]
13	France	Drinking water	2.5 ng/L	Hérault watershed	[236]
14	France	Wastewater (eff)	486 ng/L	WWTP	[229]
15	France	Wastewater (eff)	2.5 µg/L	WWTP	[228]
16	Germany	Wastewater (inf)	6.3 µg/L	WWTP in Berlin	[233]
17	Germany	Wastewater (eff)	3.0 µg/L	WWTP in Berlin	[233]
18	Germany	Wastewater (eff)	5.1 µg/L	WWTP	[237]
19	Germany	Primary sludge	7020 µg/kg	WWTP	[238]
20	Germany	Secondary sludge	310 µg/kg	WWTP	[238]
21	France	Seawater	7.7 – 63.4 ng/L	Seine estuary	[239]

22	France	Seawater	1.5 µg/L	Mediterranean sea	[236]
23	Germany	Seawater	0 - 9.2 ng/L	Baltic Sea	[240]
24	Germany	Seawater	0 - 6.2 ng/L	North Sea	[241]

The management of pharmaceuticals such as DCF in wastewater is particularly challenging as these pollutants are often only partially eliminated in WWTPs. Studies on the fate of DCF in WWTPs are often inconclusive or contradictory [215]. In fact, DCF elimination rates have been found in the range of 0 – 80%, with most values in the 20-40% interval. The reasons for these low elimination rates are poor biodegradability of DCF on one side and the low DCF-adsorption ability of sewage sludge on the other side. Although high concentrations of DCF can be found adsorbed on sludge (Table 3, entries 19/20), a considerable fraction is still present in the effluents of WWTPs. Both factors result in the presence of considerable amounts of DCF in WWTP effluents. In this way, DCF continuously enter the aquatic system via the surface water input (Table 3, entries 16/17), thus resulting in a permanent contamination of surface and ground water.

These results show that innovative water treatment techniques have to be developed in order to reduce the presence of pharmaceuticals in the effluents of WWTPs. These techniques can be for example membrane-bioreactor technologies. Additionally, the process parameters for wastewater treatment can be adapted in view of more efficient DCF mineralization. As an example, longer solid retention times (SRT) and longer hydraulic retention times (HRT) result in higher DCF elimination rates, but are hardly compatible with standard treatment processes applied in WWTPs. Biodegradation can also be enhanced using microorganisms capable to degrade DCF. These results indicate that the management of pharmaceuticals in the aquatic environment is a complex issue and further research is needed to find valuable strategies allowing for an efficient and complete transformation and/or degradation of these compounds in WWTPs and DWTPs [215].

To sum up, DCF can be found in nearly all water bodies. It enters the aquatic environment often via its import through surface water. An important aspect is the low elimination rate of DCF in

WWTPs which is due to its poor biodegradability. DCF is neither efficiently mineralized nor efficiently adsorbed on sewage sludge. However, regarding this latter aspect, pH is a crucial factor. Elimination of DCF on sludge is strongly enhanced in slightly acidic media compared to neutral media. The adsorption of DCF in its protonated neutral form seems to be favored compared to the separation of the anionic carboxylate species [238, 242].

The omnipresence of DCF represents a high environmental risk particularly due to its interactive effects with other types of environmental pollutants such as pharmaceuticals, pesticides, personal health products and metallic contaminants. The occurrence of all these pollutants together with DCF in particular in wastewater may give rise to synergistic effects affecting the whole aquatic life [8, 243]. The monitoring of DCF, together with other emerging contaminants, will therefore become a challenge in water treatment in the near future.

Effective adsorbents for DCF removal

DCF is an omnipresent compound, and efficient strategies for its removal are required. Various novel strategies for DCF removal from wastewater have recently been investigated, including physical processes (adsorption, coagulation flocculation), biological (i.e. microbial or enzymatic) degradation and biotransformation, and chemical strategies such as electrochemical degradation and photolytic/photocatalytic degradation [8, 215]. As an example, DCF can efficiently be degraded photolytically [244] via irradiation with UV light. The photodegradation can be assisted by the presence of photocatalytic materials such as titanium dioxide [245, 246] or TiO₂-WO₃ mixed oxides [247].

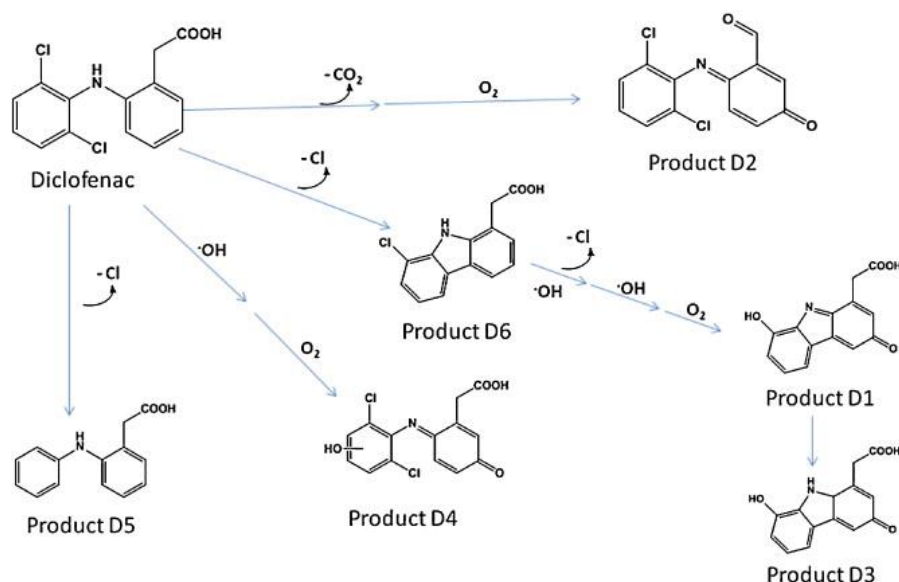


Figure 14. Photodegradation products of DCF. Reprinted from ref. [244] with permission.

Photodegradation is often combined with advanced oxidation processes (AOP) to transform organic pollutants into biodegradable intermediates. In this context, ozonisation using strong oxidizing agents such as H_2O_2 appeared as a suitable strategy for the mineralization for a large panel of organic pollutants such as DCF [248]. However, both the degradation of DCF via photolytic or oxidation pathways results in the formation of a large panel of organic degradation products [249] whose ecotoxicity needs to be assessed as well, Figure 14.

On the other side, DCF can be separated from wastewater *via* solid-liquid extraction processes using a large variety of adsorbent materials. Sequestration is an important method for the removal of DCF from water bodies, as other methods are either inefficient (biological degradation, adsorption on sewage sludge) or result in the formation of degradation products (photodegradation, oxidation processes).

A multitude of adsorbents has therefore been studied for DCF adsorption, including metal-organic frameworks [250], activated carbons [251], graphene oxide [252], biomass [253] and biopolymers such as chitosan [254], clays and double layered hydroxides [255, 256] and finally silicas, organosilicas and silica supported ionic liquids [257-260]. Due to the chemical characteristics of DCF, its adsorption can be triggered by hydrophobic interactions, π - π stacking interaction, or ionic

interactions. Anion exchange materials seem to be particularly well suited for DCF adsorption [261]. In the following, we will present the main groups of adsorbents for DCF removal from aqueous solution.

Clays only show limited adsorption capacity for DCF adsorption. However, the affinity between clays and DCF can significantly be increased via the incorporation of organic compounds. Various clays such as bentonite and halloysite have been tested as adsorbents for DCF. Bentonite is an aluminium phyllosilicate clay consisting mostly of montmorillonite. Bentonite is largely used as adsorbent for pharmaceutical micro-pollutants, because of its abundance, low cost and its suitable textural properties, i.e. exchangeable cations in the interlayer spaces. On the other side, halloysite is an abundant clay mineral belonging to the group of the 1:1 phyllosilicates. Its remarkable property is that its layers roll up in the form of hollow nanotubes that delimit spaces called lumens.

The intercalation of organic compounds such as CTAB into the interlayer space of the clay structures allows the synthesis of organoclay nanocomposites. The incorporation of CTAB in the interlayer spaces of these materials led to highly efficient DCF adsorbing materials [262, 263]. A similar approach was reported by Krajisnik, who described cetylpyridinium modified natural zeolites for DCF adsorption [264]. In all cases, hydrophobic interactions combined with an increase of the surface charge are the reasons for the increased adsorption properties of these organic-inorganic nanocomposites. The incorporation of surfactants within the interlayer spaces of clays or zeolites is crucial for the adsorption of organic pollutants and allows for a dramatic increase of the adsorption efficiency compared to the pure mineral materials.

Due to their morphological and textural properties, Metal-Organic Frameworks (MOFs) appear as very promising adsorbents for DCF adsorption. Indeed, a ZIF-67/CTAB nanocomposite has been used for the removal of DCF from aqueous media. The presence of CTAB increases the adsorption capacity of the composites as it enhances the surface charge of the material. Compared to the pure ZIF-67 material, the nanocomposite with CTAB shows a ten times higher adsorption capacity for DCF [265].

Other MOFs have also been used for DCF removal and high adsorption capacities up to 263 mg/g of MOF were observed. The chemical nature of the adsorbent, i.e. the functionalization with ionic groups, together with the adsorption conditions (pH of the liquid media, contact time, etc.) are crucial to achieve high adsorption efficiencies. For example, the highest adsorption capacities have been found for amine and sulfonate functionalized UiO-66. These results may be explained by some particular adsorbent-adsorbate interactions, such as base–base repulsion, or acid–base attraction involving the amine and carboxylate groups of DCF and the amine and sulfonate groups of the MOF-adsorbent [266]. More recently, a porous Cu-based MOF showed extraordinary high adsorption capacity of up to 900 mg/g [267].

Another important class of adsorbents are carbon based materials such as activated carbons (ACs), graphene and graphene oxide. ACs are widely used as adsorbents, both on the laboratory scale and for industrial uses. ACs have also been investigated for the removal of NSAID and in particular of DCF from aqueous solution. Due to the different chemical nature, the adsorption mechanism is mostly based on weak interactions such as van-der Waals bonding or π - π stacking interactions. However, activated carbons sometimes also show high adsorption capacity of DCF up to 400 mg/g [205, 226].

Various other types of carbon based materials have been used for DCF adsorption purposes. In a combination of ACs and MOFs, MOFs have also been used to access porous carbonaceous materials via pyrolysis. This approach leads to so-called PCDMs (porous carbons derived from MOFs). These solids display high adsorption capacities for DCF especially compared to conventional porous carbons [268-270]. Finally, graphene oxide is another promising adsorbent for DCF due to π - π stacking interactions with the aromatic rings of DCF [252].

Porous silicas, ionosilicas and silica supported ionic liquid phases (SILPs) are among the most polyvalent and tuneable functional materials, as silica offers a large variety of possibilities for processing and morphology control, and ionic liquids (ILs) allow for the fine-tuning of the physico-chemical properties of the materials, such as hydrophilicity/hydrophobicity and ionic interactions.

These materials are therefore particularly suitable for the elaboration of ion exchange materials. In fact, porous thiol and amine functionalized silica adsorb DCF more efficiently than the parent pristine silica. This effect is mainly due to hydrophobic interactions [271].

On the other hand, the incorporation of ionic sites within the material gives rise to silica based ion exchange materials. These ionosilicas and SILPs are versatile adsorbents for anionic drugs displaying high adsorption capacities up to 600 mg/g [257, 260]. The polyvalence of these materials is highlighted by the fact that the adsorption process can be controlled by the counter anion [257]. This feature shows that ionosilicas and SILPs are particularly universal adsorbent phases and offer multiple ways of chemical modification in view of a fine-tuning of the interfacial properties.

Renewable materials such as bagasse or biopolymers such as chitosan have also successfully been used for DCF removal from aqueous solution. For example, Isabel grape (*Vitis labrusca* x *Vitis vinifera*) bagasse was tested as a low cost adsorbent. Despite the fact that the adsorption performances of bagasse are considerably lower compared to other materials (maximum capacity < 50 mg/g), bagasse appears as a good solution for water treatment and DCF sequestration due to its large scale availability and its insignificant commercial value, thus compensating its lower efficiency [253]. Recently, bagasse-based PET/Fe(III) containing nanocomposites were also successfully used for DCF adsorption [272], highlighting the potential of these low-cost adsorbents in water treatment. Regarding functional biopolymers, Liang et al. reported a chitosan/iron oxide nanocomposite displaying high DCF adsorption capacity of nearly 470 mg DCF/g of material [273]. The material can be recovered in a magnetic field due to the presence of magnetic Fe₃O₄ and re-used in at least four adsorption-regeneration cycles while maintaining a DCF removal efficiency of 70%.

All these examples show that multiple types of materials with good to excellent DCF adsorption performances exist, including inorganic, hybrid and purely organic materials. The observed adsorption capacities are sometimes very high and can reach more than 600 mg DCF/g of adsorbent, but these results are often compromised by the presence of competing anionic species such as chloride or carbonate, or other organic anionic species. In view of an efficient re-use of these

adsorbents, closed adsorption-desorption cycles and regeneration of these often costly adsorbents have to be investigated. Furthermore, it has to be mentioned that most of these studies are carried out under laboratory conditions. The efficiencies of these materials under real life conditions is still a rather unexplored field and has to be addressed before transposition on wastewater treatment under real large scale applications.

Finally, it has to be pointed out that rather minor changes in wastewater treatment have enormous effects on the elimination rates of DCF in WWTPs. Slight pH changes allow for a twenty-fold increase of the DCF elimination rate. Other parameters such as resident times need also to be addressed for a more efficient elimination of DCF in particular, but all other organic anionic species from wastewater in general [215].

In summary, this subsection shows that DCF is present in almost all water bodies and even in tap and drinking water, in concentrations in a range of several ng/L to µg/L. The omnipresence of DCF is due to ineffective treatment strategies in WWTPs and DWTPs, and related to the poor biodegradability and very low adsorption of anionic compounds on sewage sludge, combined with high mobility due to high water solubility of DCF-sodium. The removal of DCF from wastewater in WWTP is therefore often inefficient. Although DCF has a relatively short elimination half-life in freshwater, it enters the aquatic environment as a pseudo-persistent trace pollutant due to continuous input. DCF can therefore be found in nearly all water bodies, starting from surface water, ground water, and even in drinking water. As DCF is also present in the marine environment, it was also found in marine organisms such as mussels and fish (Figure 15).

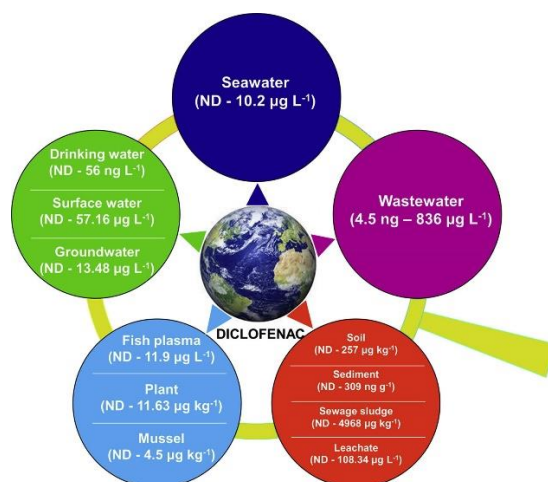


Figure 15. Global occurrence of diclofenac range in various environmental matrices. ND: not detected. Reprinted from ref.[9] with permission.

All these findings clearly indicate that continuous monitoring of DCF and other pharmaceutically active compounds (PhACs) and, more generally, Pharmaceutical and Personal Care Products (PPCPs) in the aquatic environment is necessary [274]. Furthermore, novel techniques and strategies for an efficient removal of these compounds from all water bodies are required. Regarding DCF, three main strategies are of importance for a more efficient removal of DCF from wastewater during conventional wastewater treatment:

- process optimization in wastewater treatment, namely longer hydraulic residence times, leading to longer contact times of DCF with biomass
- enrichment of DCF-metabolizing microorganisms in the bioreactor
- pre-treatment of wastewater using (photo)oxidation methods.

However, as all these method require drastic process modifications, are often time consuming, not always efficient and result in the contamination with secondary products originating from DCF degradation, adsorption techniques for the sequestration of DCF from wastewater are of particular importance and need further investigation to reach acceptable DCF concentrations in WWTP effluents.

11.5 Final Observations

At this point, it is quite fair to say that only innovation in oxoanion sequestration is not enough to combat environmental pollution: while many industries are responsible for significant pollution, they also provide employment, resources, and resources that are needed, especially in developing countries [275]. Therefore, it is the environmental authorities of many countries especially the least developed and developing countries, are under enormous pressure to control and reduce pollution on many levels [276]. It is clear that besides technological advances, (environmental) education plays a vital role in improving the overall conditions of the populations in these countries [277]. Therefore, raising awareness through continuous consultation, focus group discussion, and environmental education has to be put in place in these countries to ensure that the people involved in different industries and local stakeholders recognize the alarming threat [278, 279]. It is also necessary that employers, laborers and management of these industries consider adopting certain strategies reducing the overall health risk that are the consequences of untreated wastewater discharge. Educational workshops and training must be in place to educate the relevant industries to understand and implement necessary cleanup methods such as sequestration. These efforts must be backed by systematic counseling with the local stakeholders to further support the development of a deeper understand of the threats of uncontrolled wastewater pollution. The same efforts must also highlight the benefit of feasible treatment planning and reorganization of water treatment [280].

Clearly, changing the approaches of industrial setting in the developing will not take place overnight. However, it is absolutely necessary that continuous training on all levels (schools, universities, industries, public stakeholders) is established and that better pollutant management plans are put in action. Local pressure groups, environmental activists, governments and other environmental authorities are obvious partners in these developments [281].

Environmental education has been recognized as silver bullet to build more environmentally aware populations [282]. Typically, the problem of environmental pollution mitigates with well-informed citizens and schools and universities are highly suitable platforms to educate but also train scientists,

engineers and decision makers [278]. Among others, demonstration experiments and small scale live demonstration of pollutant removal using hands-on in schools, universities and any other public event that is accessible for education should be a useful tool for establishing an understanding of the issues and chances of water treatment for any society [283].

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