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铁氧化物-二价铁体系在潜流带低渗透区的氧化还原特性研究进展

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摘要: 潜流带是河流与地下水交互的关键带，具有非均质性，其中低渗透区富含的铁氧化物，在污染物的非生物自然衰减过程中发挥着重要作用。本文从铁氧化物和溶解性二价铁 $Fe(Ⅱ)_{aq}$ 的共存体系出发，评述了该体系的氧化还原能力及影响因素，并以地下水中常见的污染物氯代烃为例阐述了铁氧化物-$Fe(Ⅱ)_{aq}$ 体系在氯代烃非生物自然衰减中的作用。指出铁氧化物-$Fe(Ⅱ)_{aq}$ 体系的还原能力可用氧化还原电位(Eh)表示，Eh 的大小受 pH 值、温度、溶解氧(DO)、溶解性二价铁浓度、无机和有机配体等因素的影响，可用来定量描述氯代烃等污染物被还原的速率常数。目前铁氧化物-$Fe(Ⅱ)_{aq}$ 体系 Eh 的快速测定、含水层中铁氧化物种类和含量、不同铁氧化物共存和复杂水化学条件下 Eh 与氯代烃等污染物还原速率常数之间的关系，是准确评估污染物非生物自然衰减能力和程度的重要内容。

关键词: 潜流带；铁氧化物；非均质性；非生物自然衰减

要点:

(1) 河流与地下水交互的潜流带存在富含铁氧化物的低渗透区，是污染物赋存和转化的场所。

(2) 低渗透区铁氧化物-$Fe(Ⅱ)_{aq}$ 的还原能力强于氧化物或者液相二价铁单独存在的体系。

(3) 氯代烃非生物自然衰减速率可用铁氧化物-$Fe(Ⅱ)_{aq}$ 体系的 Eh 定量描述。

中图分类号: O614.811　　**文献标识码:** A

潜流带是河流与地下水交互的关键部位。潜流交换过程中, 多种物质、养分和能量进行输移, 水体中的溶解性成分发生迁移和转化。同时潜流带由不同粒径的沉积物组成, 形成了潜流带的一项基本属性——非均质性。潜流带中由细颗粒构成的低渗透区富含铁矿物, 水环境中的铁元素对氧化还原条件十分敏感, 地表水和地下水随着水位和空间位置的变化进行不同程度的交互, 进而引起温度、溶解氧(DO)和溶质组分的动态变化, 溶解性铁和含铁矿物之间的动态平衡将被打破, 影响与铁相关的生物地球化学过程。

在天然条件下, 地下水和潜流带的低渗透区处于缺氧环境, 溶解性的铁主要以二价铁形式存在, 其形态包括与羟基和水分子不同程度结合的络合态, 因而将溶解态的二价铁用 $Fe(Ⅱ)_{aq}$ 来表达。含水层介质中铁氧化物的主要种类有针铁矿、磁铁矿、赤铁矿和水铁矿等。研究表明, 铁氧化物的存在可以显著增强 $Fe(Ⅱ)_{aq}$ 的还原性, 表现为提高了污染物降解

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的速率常数[1-2]，这一现象得到了研究者的广泛关注，分别从铁氧化物表面吸附态二价铁的浓度、铁氧化物的结构、$E_{\mathrm{Fe^{3+}/Fe^{2+}}}$和污染物线性自由能等方面进行研究和探讨[3-4]，得出一些有意义的结论，特别是 Stewart 等[3]和 Li 等[5]发现硝基苯的还原速率常数与溶液中 Eh 和 pH 具有相关关系的认识。但是，这些认识是利用批实验在非常简单的水化学条件和单一的铁矿物中完成的，与实际的含水层介质组成、水化学成分和水动力条件具有较大差异，尤其是在 DO 变化比较大的潜流带，铁氧化物与 Fe(Ⅱ)$_{aq}$ 对污染物还原降解的机理仍不清晰，其发生的条件及影响因素还需开展进一步研究。

本文从潜流带富含铁氧化物的低渗透带角度，总结铁氧化物和溶解性二价铁共存体系的还原能力(Eh)，梳理影响其还原能力的因素，同时以典型的可还原污染物——氯代烃为例，分析铁氧化物-Fe(Ⅱ)$_{aq}$ 体系在污染物非生物自然衰减中的作用，指出目前亟需开展的研究内容，为野外尺度定量评估污染物非生物自然衰减的可能性和程度提供理论支撑。

1 铁氧化物-Fe(Ⅱ)$_{aq}$ 的还原能力

地下水中铁的来源主要是地下水与含水层介质的水岩相互作用。通常铁矿物在水溶液中的溶解和沉淀遵循两条规律：①氧化条件促使铁沉淀，还原条件促使铁溶解；②碱性条件促使铁沉淀，酸性条件促使铁溶解。在含水层处于强还原环境时，三价铁矿物被还原溶解为 Fe(Ⅱ)$_{aq}$，特别是当有淤泥夹层时，由于有机质的存在和微生物的活动，降低了 pH 值，提高了铁氧化物的溶解度，更有利于溶解性铁在水中的富集。

1.1 含水介质中的铁氧化物与溶解性二价铁 Fe(Ⅱ)$_{aq}$ 赋存的多样性

自然界中各种类型的岩石和矿物中的铁含量差异很大[6]，地下水中 Fe(Ⅱ)$_{aq}$ 的浓度与其流经地区的岩石和矿物的类型密切相关。环境中主要的铁氧化物有 16 种 (表 1[7])，针铁矿和赤铁矿是土壤和沉积物中最常见的铁氧化物。针铁矿在凉爽、潮湿的环境中有较高的丰度，在温暖地区与赤铁矿共存，在寒冷地区与水铁矿或纤铁矿共存。赤铁矿常见于热带和亚热带地区，可与针铁矿胶结。而无定形的水铁矿稳定性较差[8]，在热带、亚热带气候下易转变为赤铁矿，在潮湿的温带气候下易转变为针铁矿[9]。

地下水中 Fe(Ⅱ)$_{aq}$ 含量随含水介质粒径的减小而升高。在第四系含水层中，尤其是在淤泥质、细颗粒含水层中溶解性铁分布广泛，因而地下水中污染物的归宿和自然衰减研究应考虑铁氧化物和 Fe(Ⅱ)$_{aq}$ 共存的非均相体系 (图 1)。

通常，铁的氧化物和氢氧化物统称为铁的氧化物。铁的氧化物在水环境中广泛存在并参与众多还原反应[10-11]，同时铁氧化物产生的 Fe(Ⅱ)$_{aq}$ 也可以将污染物非生物还原，因而这些还原反应对于地下水中污染物的非生物衰减与修复十分重要，地下水中污染物包括了以 TCE(三氯乙烯)为代表的氯代有机溶剂、放射性元素[12]、有毒有害的金属及其氧化物[13-14]和农药[15-16]。污染物被还原的速率和程度取决于 Fe(Ⅱ)$_{aq}$ 的浓度和形态[17]，研究发现铁氧化物表面结合态的 Fe(Ⅱ) 比溶液中单独存在的 Fe(Ⅱ) 对污染物的还原速率更快[18]，这个体系称为铁氧化物-Fe(Ⅱ)$_{aq}$ 体系。

表 1 常见铁氧化物的类型

Table 1 Types of common iron oxides.

氧化铁		水合羟基氧化铁	
化学式	铁氧化物	化学式	铁氧化物
β-Fe_2O_3	β-Fe_2O_3	$Fe_5HO_8 \cdot 4H_2O$	水铁矿
ε-Fe_2O_3	ε-Fe_2O_3	α-FeOOH	针铁矿
FeO	方铁矿	γ-FeOOH	纤铁矿
Fe_3O_4	磁铁矿	β-FeOOH	四方纤铁矿
γ-Fe_3O_4	磁赤铁矿	δ’-FeOOH(结晶度低)	六方纤铁矿
α-Fe_2O_3	赤铁矿	δ-FeOOH(结晶度高)	六方纤铁矿
		$Fe_{16}O_{16}(OH)_y(SO_4)_x \cdot nH_2O$	施氏矿物
		$Fe(OH)_3$	纳伯尔矿
		$Fe_x^{\mathrm{III}}Fe_y^{\mathrm{II}}(OH)_{3x+2y-z}(A^-)_z$ ($A=Cl^-$; $1/2CO_3^{2-}$; $1/2SO_4^{2-}$)	绿锈

注：修改自杨忠兰等 (2021)[7]。

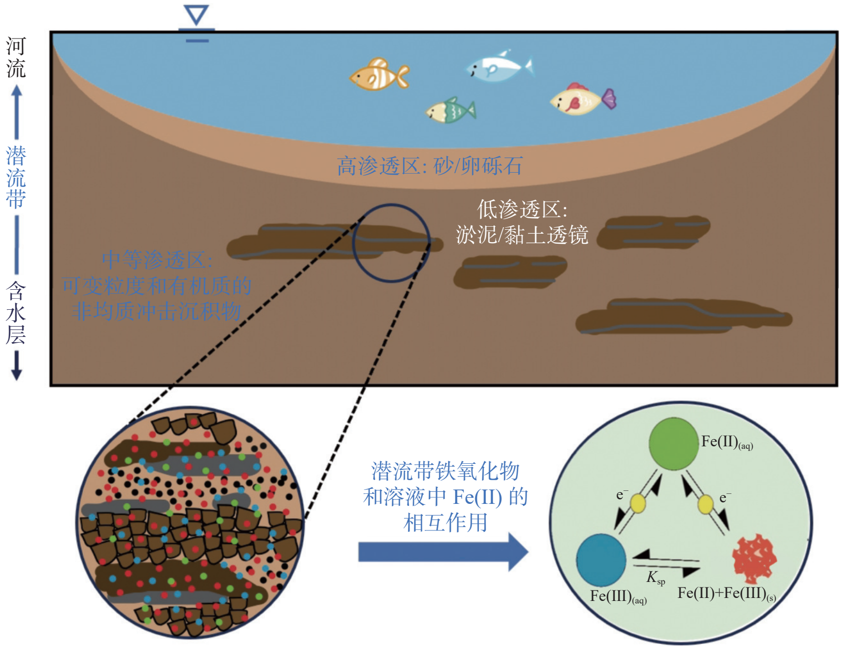

图1　潜流带的非均质性与铁矿物-Fe(Ⅱ)$_{aq}$ 体系

Fig. 1　Heterogeneity and iron-Fe(Ⅱ)$_{aq}$ system of hyporheic zones.

1.2　铁氧化物- Fe(Ⅱ)$_{aq}$ 非均相体系还原能力增强的机理

当有铁氧化物存在时，Fe(Ⅱ)$_{aq}$ 对污染物的还原能力得到明显增强[19-22]。早期研究认为，这种现象是由于溶液中 Fe(Ⅱ) 吸附在铁氧化物上，使铁氧化物表面具有更高的电子密度，同时铁氧化物表面的羟基配体也可作为电子供体[23]，因而铁氧化物和溶解态 Fe(Ⅱ) 共存时，其溶液的 Eh 表现为更低[24-25]。但后续研究认为上述解释是不合理的，首先光谱学和微形貌学研究表明，溶液中 Fe(Ⅱ) 很难在铁氧化物表面形成稳定的吸附态，而是被氧化成 Fe(Ⅲ)，贡献了一个电子进入半导体铁氧化物的晶格内[26]；其次，上述解释中认为铁氧化物- Fe(Ⅱ)$_{aq}$ 处于热力学不平衡状态，但是电化学测量表明，铁氧化物结合的 Fe(Ⅱ) 和溶液中的 Fe(Ⅱ) 具有固定的 Eh 值[27]，处于热力学平衡状态。此外，关于铁氧化物增强 Fe(Ⅱ)$_{aq}$ 对污染物还原能力的现象还有另外一种假设，认为铁氧化物的存在改变了溶液中 Fe(Ⅱ) 被氧化的产物，进而影响反应的吉布斯自由能[28]。在缺氧条件下，即在潜流带的低渗透区域，溶液中 Fe(Ⅱ) 被氧化生成 Fe(Ⅲ) 的配合物或者亚稳态的铁氧化物附着在铁氧化物晶体表面时，溶液中 Fe(Ⅱ) 会通过晶体增长被氧化成针铁矿或者赤铁矿等热力学稳定的铁氧化物[29]，这是一个能量释放的过程，具有更负的吉布斯自由能[30]。这种情况下，如果污染物去除时发生电子转移，理论上，铁氧化物-Fe(Ⅱ)$_{aq}$ 体系的 Eh 可以用来估计污染物去除的速率常数 (K_{obs})[31]。这个观点在去除硝基苯等污染物的反应中得到了验证[32]，但是 TCE 等污染物被还原过程中，由于发生多步电子转移，Eh 的变化与污染物被还原的 K_{obs} 之间的定量关系还需进一步检验。

1.3　铁氧化物-Fe(Ⅱ)$_{aq}$ 体系还原能力的影响因素

环境中影响缺氧区铁氧化物-Fe(Ⅱ)$_{aq}$ 体系还原活性的因素有很多[33]，包括 pH[34]、溶解性 Fe(Ⅱ) 浓度[24]、Fe(Ⅱ) 在铁氧化物表面的形态[35]和铁氧化物的种类[36]。其中溶液 pH、溶解性 Fe(Ⅱ) 浓度和 Fe(Ⅱ) 在铁氧化物表面的形态是影响污染物还原动力学的主要因素[37]。此外，研究发现当存在无机配体和天然有机质 (Natural organic matter, NOM) 时，铁氧化物和 Fe(Ⅱ)$_{aq}$ 体系的还原活性也受到不同程度的影响[15]。在针铁矿 Fe(Ⅱ)$_{aq}$ 体系还原能力研究中[38]，尽管磷酸盐对电子转移没有任何影响，但有机磷酸酯的吸附可以完全阻断电子的传递；也有研究发现硅酸盐阻碍了三价铁矿物和 Fe(Ⅱ)$_{aq}$ 之间的电子传递，并认为是由于硅酸盐在矿物表面的吸附抑制了液相 Fe(Ⅱ) 与矿物表面的接触[39]。Hinkle 等[40]证明了磷酸盐和硫酸盐可以提高 Fe(Ⅱ) 在铁氧化物表面的吸附，并提出两个互为矛盾的推断：①液相的 Fe(Ⅱ) 由于被铁氧化物吸附致使界面浓度升高而推动了体系的还原活性；

②氧化物表面的配体使 Fe(Ⅱ)稳定化而阻碍电子转移。因此哪一个推断是正确的,还需进一步研究。

除了无机配体,NOM 也会阻碍铁氧化物-Fe(Ⅱ)$_{\mathrm{aq}}$体系的还原活性。主要原因一方面在于 NOM 的吸附屏蔽了污染物接触 Fe(Ⅱ)的活性位点,另一方面在于 NOM 竞争或者氧化了铁氧化物表面的 Fe(Ⅱ)。有学者研究表明,铁氧化物-Fe(Ⅱ)$_{\mathrm{aq}}$体系的还原活性和 8 种 NOM 的分子量、羧基含量、碳氧氮元素的比例、饱和度和芳香度等理化性质密切相关[41]。其中,小分子羧酸盐作为 NOM 的主要代表类型,无论是人为源还是天然源都是含水层中重要的配体类型[42-43],它们无论在溶液中还是在氧化物表面都易形成络合物[44],因此小分子羧酸盐影响铁氧化物的溶解、风化等地球化学过程和污染物在环境中的归趋[45]。但是,当存在某种小分子羧酸盐时,对铁氧化物表面形态以及配体如何影响铁氧化物-Fe(Ⅱ)$_{\mathrm{aq}}$体系还原活性的认识仍是不全面的。

2 潜流带中铁氧化物-Fe(Ⅱ)$_{\mathrm{aq}}$对污染物的非生物衰减

潜流带中广泛存在的铁氧化物-Fe(Ⅱ)$_{\mathrm{aq}}$体系对污染物的化学还原过程是污染物非生物自然衰减的主要过程,氯代烃是地下水中典型的有机污染物,在地下水向地表水补给过程中,更容易滞留在潜流带的低渗透区。铁矿物还原引起的氯代烃非生物降解是该类污染物自然衰减的重要组成部分[46-47],非生物自然衰减反应尽管很慢,但对于地下水修复的时间尺度(一般为十几年或者几十年)仍然具有重要意义[48]。如此慢的反应速度在实验室研究的时间尺度下(一般为几个月,最多为几年)很难去模拟[17,49],即使是在污染场地也是不容易量化的。

2.1 铁矿物还原氯代烃的途径

实验室模拟实验证明了氯代有机溶剂非生物自然衰减(Abiotic natural attenuation, ANA)的可能性[50-51],磁化率和 X 射线衍射矿物学表征也提供了佐证[52],但是预测 ANA 反应速率仍然困难。研究者逐步认识到氯代烃 ANA 的过程比预期要复杂[52],且矿物相是此过程中非常重要的因素,特别是与 Fe(Ⅱ)$_{\mathrm{aq}}$浓度相关的新矿相[19,53]。这种新矿相被定义为反应活性矿物中间体(Reactive mineral intermediates, RMIs),在 ANA 过程中不断地生成和消耗。

氯代烃被还原性铁氧化物通过还原消去、氢解、脱氢卤和水解的途径进行非生物衰减(图 2),某些降解产物(如乙炔)可以作为非生物反应的标志物。不同矿物对氯代烃的还原能力不同,其还原速率受到 pH 等环境因素的影响。同一种矿物去除同一种氯代溶剂,其反应速率常数由于 pH、缓冲溶液、合成方法等实验条件不同可以相差几个数量级。例如,He 等[54]发现矿物合成时是否冻干会造成去除 TCE 的速率常数在相同实验条件下相差一个数量级。

2.2 氯代烃非生物衰减的野外证据

到目前为止,还没有一种可行的方法去定量刻画野外尺度的非生物自然衰减,只能采用多种方法互相补充和验证才能进行间接判断[55]。多数情况下,研究者会在地下水流线上利用污染物及其产物的质量平衡模型进行计算来获取最为直接的证据,这个过程需要精细化的监测提供数据支撑[1,56],但是模拟计算的结果常常是不确定的[48,57]。虽然单体同位素分析技术(Compound specific isotope analysis, CSIA)可作为非生物自然衰减的诊断方法,但其结果的解译由于多种竞争反应并存引起的同位素富集因子漂移而变得非常复杂[50]。

在野外尺度上,影响氯代烃非生物衰减的关键因素是含水层介质中还原性矿物的含量[58],野外调查发现 0.5% 的活性矿物含量足以引起氯代烃的非生物衰减,也有学者发现 Fe(0) 系统孔隙中形成的氢氧化物与 Fe(Ⅱ)之间的协同作用是污染物被还原的主要机制[59]。

在特定条件下,非生物反应对于自然衰减的贡献是不可忽略的,尤其是含水层中能够引起氯代烃还原的矿物含量比较高时,非生物衰减的贡献尤为重要。在野外尺度上,不同矿物能够引起氯代烃非生物自然衰减的最小含量数据十分匮乏,不同矿物引起氯代烃非生物自然衰减的速率常数信息也很有限。如果可以通过实验、调查或者收集分析资料获得上述信息,基于这些信息的水文地球化学模型可以将非生物自然衰减的速率常数与水文地质参数和水化学参数关联起来,在一定程度上对于预测氯代烃的非生物自然衰减是非常有价值的。

3 结语与展望

在适当的水文地球化学条件下,自然发生的非生物还原是 TCE 等可还原污染物监测自然衰减修复策略不可分割的部分。在潜流带等特定条件下,污染物非生物自然衰减发生的可能性和程度取决于铁氧化物-Fe(Ⅱ)$_{\mathrm{aq}}$的还原能力,而这种还原能力与铁氧

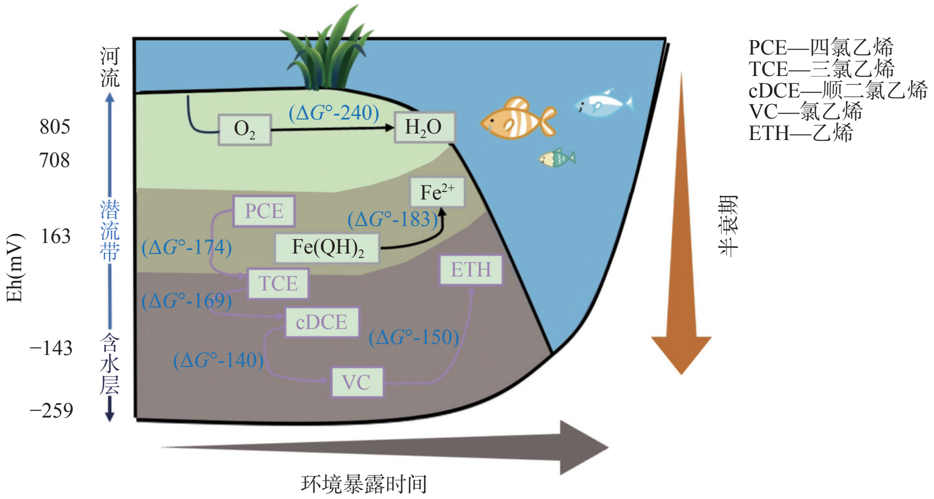

图2　潜流带典型氯代烃 (四氯乙烯) 与铁矿物- Fe(Ⅱ) 的氧化还原势

Fig. 2　Redox potential of typical chlorinated hydrocarbons (tetrachloroethylene) and iron mineral-Fe(Ⅱ)$_{aq}$ in the hyporheic zones.

化物的种类及含量、pH、DO、溶解性二价铁的浓度以及其他水化学参数相关。

由于含水层中铁矿物的种类和水化学条件是复杂的, 本文认为在以下几个方面仍亟需进行深入研究: ①快速且准确地测定铁氧化物-Fe(Ⅱ)$_{aq}$ 非均相体系氧化还原电位(Eh); ②铁氧化物-Fe(Ⅱ)$_{aq}$ 体系对污染物还原的动力学机理; ③污染物非生物自然衰减的定量评估。这些研究可为含水层中污染物修复策略的制定和风险管理的实施提供理论依据和技术支撑。

Progress on Redox Characteristics of an Iron Oxide-Ferrous System in the Hyporheic Zone

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HIGHLIGHTS

(1) The hyporheic zone where rivers interact with groundwater exists in the low permeability zone rich in iron oxide, which is the place where pollutants occur and transform.

(2) The reduction capacity of iron oxide-Fe(Ⅱ)$_{aq}$ in the low-permeability zone is stronger than the individual systems of oxide or aqueous phase ferrous.

(3) The abiotic natural attenuation rate of chlorohydrocarbon can be quantitatively described by Eh of iron oxide-Fe(Ⅱ)$_{aq}$ system.

ABSTRACT: The hyporheic zone is a critical zone for the interaction between groundwater and surface water. The heterogeneous system composed of iron oxides and ferrous in the low-permeability zone of the hyporheic zone is vital for the abiotic natural attenuation of pollutants. This review summarized the universality, reduction ability, and influencing factors of the iron oxides and ferrous in groundwater. Chlorinated hydrocarbons are taken as typical pollutants to indicate the role of iron oxide and ferrous system in their abiotic natural attenuation process. The review indicates that the reducing ability of the iron oxide and ferrous system can be expressed by Eh which is influenced by pH, ferrous concentration, and natural organic matter. Whereas the rate constant of abiotic natural attenuation of pollutants can be quantitatively described by Eh. So far, the rapid and accurate determination of Eh and the establishment of quantitative relationships between various pollutants and Eh under complex hydrochemical conditions will be the key to evaluating the abiotic natural attenuation of pollutants in aquifers. The BRIEF REPORT is available for this paper at http://www.ykcs.ac.cn/en/article/doi/10.15898/j.ykcs.202309090150.

KEY WORDS: hyporheic zone; iron oxides; heterogeneity; abiotic natural attenuation

BRIEF REPORT

The hyporheic zone is a crucial area for the interaction between rivers and groundwater. The low-permeability zone of the hyporheic zone is composed of fine particles which are rich in iron minerals. Surface water and groundwater interact to varying degrees with changes in water level and spatial location. The equilibrium between soluble iron and mineral-bearing iron is disrupted and affects iron biogeochemical processes. Under natural conditions, soluble iron mainly exists in different forms of divalent iron in the subsurface environment, expressed as $\mathrm{Fe(II)_{aq}}$. Research shows that iron oxides in aquifers can significantly enhance the reducibility of $\mathrm{Fe(II)_{aq}}$, which is expressed by the increase of the rate constant of pollutant reduction and degradation[1-2]. Stewart et al.[3] and Li et al.[5] obtained a relationship between the reduction rate constant of nitrobenzene and the Eh and pH of the iron oxide-$\mathrm{Fe(II)_{aq}}$. However, these insights were obtained through batch experiments under very simple hydrochemical conditions and a single iron mineral, which differ significantly from the actual composition of the aquifer medium, hydrochemical composition, and hydrodynamic conditions. Especially in the hyporheic zone with significant changes in dissolved oxygen (DO), the mechanism of the reduction and degradation of pollutants by iron oxide and $\mathrm{Fe(II)_{aq}}$ is still unclear. The conditions and influencing factors for their occurrence need to be studied further. The results of these studies can provide theoretical support for the quantitative evaluation of the possibility and degree of abiotic natural attenuation (ANA) of pollutants in the field. This review starts with the low-permeability part with iron oxides in the hyporheic zone, summarizes the reduction ability (Eh) of the coexistence system of iron oxides and soluble divalent iron, and sorts out the influencing factors of its reduction ability. At the same time, taking chlorinated hydrocarbons as an example, the role of the iron oxide-$\mathrm{Fe(II)_{aq}}$ in the ANA of pollutants is analyzed.

Usually, both iron oxides and hydroxides are collectively known as iron oxides. Iron oxides are widely present in water environments and participate in numerous reduction reactions[10-11]. The $\mathrm{Fe(II)_{aq}}$ can also reduce pollutants. Therefore, these reduction reactions are crucial for the abiotic attenuation and remediation of pollutants in groundwater. The rate and degree of pollutant reduction depend on the concentration and form of $\mathrm{Fe(II)_{aq}}$[17]. Fe(Ⅱ) in the bound state on the surface of iron oxides has a faster reduction rate of pollutants than Fe(Ⅱ) alone in solution[18]. This system is called the iron oxide-$\mathrm{Fe(II)_{aq}}$ system. The Eh of the iron oxide-$\mathrm{Fe(II)_{aq}}$ can be used to estimate the rate constant (K_{obs}) of pollutant removal[31], which has been validated in the reaction of removing nitrobenzene and other pollutants[32]. However, during the reduction process of TCE and other pollutants, due to multi-step electron transfer, the quantitative relationship between Eh and the reduced K_{obs} of pollutants still needs further examination. The pH of the solution, the concentration of soluble Fe(Ⅱ), and the morphology of Fe(Ⅱ) on the surface of iron oxides are the main factors affecting the reduction of pollutants by iron oxide-$\mathrm{Fe(II)_{aq}}$[37].

Moreover, small-molecule carboxylates also affect the dissolution, weathering, and other geochemical processes of iron oxides, as well as the fate of pollutants in the environment[45].

The abiotic natural degradation of chlorinated hydrocarbons caused by the reduction of iron minerals is an important part of the natural attenuation of such pollutants[46-47]. Although the abiotic natural degradation reaction is rather slow, it still has significant implications for the time scale of groundwater remediation (usually over a decade or several decades)[48]. Laboratory studies have demonstrated the possibility of ANA of chlorinated organic solvents[50-51], which is more complex than expected[52]. The mineral is a crucial factor in this process, especially the new mineral phase related to Fe(Ⅱ)$_{aq}$ concentration[19,53]. This new mineral phase is defined as reactive mineral intermediates (RMIs), which are continuously generated and consumed during the ANA process. Field investigations have found that 0.5% active mineral content is sufficient to cause abiotic decay of chlorinated hydrocarbons. Under specific conditions, the contribution of abiotic reactions to natural attenuation cannot be ignored, especially when the mineral content that can cause reduction of chlorinated hydrocarbons in aquifers is relatively high, the contribution of abiotic attenuation is particularly important. The possibility and degree of ANA of pollutants under specific conditions such as hyporheic zone depend on the Eh of iron oxide-Fe(Ⅱ)$_{aq}$, which is related to the type and content of iron oxides, pH, DO, concentration of soluble divalent iron, and other hydrochemical parameters.

Due to the complexity of the types of iron oxides and hydrochemical conditions in aquifers, there is still an urgent need for probe research in the following areas: (1) Rapid and accurate determination of the redox potential (Eh) of iron oxide-Fe(Ⅱ)$_{aq}$ heterogeneous systems; (2) The kinetic mechanism of iron oxide-Fe(Ⅱ)$_{aq}$ in reducing pollutants; (3) Quantitative evaluation of ANA of pollutants.

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