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磷酸盐对纳米二氧化钛吸附水体中重金属离子行为的影响和机理分析

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摘要: 纳米二氧化钛(nTiO$_2$)被广泛应用于去除水体中的重金属。磷酸盐作为水体中普遍存在的无机阴离子,能够对重金属离子在 nTiO$_2$ 上的吸附特征产生影响。本文聚焦磷酸盐存在条件下 nTiO$_2$ 胶体颗粒对典型重金属离子(Zn^{2+}和 Cd^{2+})的吸附行为,以电感耦合等离子体发射光谱法(ICP-OES)测定吸附平衡后水相中重金属离子的浓度。通过批量吸附实验考察不同水化学条件下(离子强度和共存阴离子),磷酸盐对 nTiO$_2$ 胶体颗粒吸附水体中 Zn^{2+}和 Cd^{2+}特征的影响规律。采用经典吸附等温线模型对实验数据进行拟合,并结合纳米颗粒的 Zeta 电位和粒径变化等表征手段揭示了相关吸附机制。研究发现:①磷酸盐的存在能有效地增强重金属在 nTiO$_2$ 上的吸附,Zn^{2+} 和 Cd^{2+} 的最大吸附量分别由 121.1mg/g 和 84.7mg/g 增加至 588.3mg/g 和 434.8mg/g,增加了 3.8~4.1 倍。这主要由于磷酸盐能够通过桥连作用形成金属-磷酸盐-nTiO$_2$ 三元络合物以及增加重金属离子和胶体颗粒之间的静电引力,从而增强 nTiO$_2$ 对重金属离子的吸附。②背景溶液中离子强度的增加会降低 nTiO$_2$ 对重金属离子的吸附效果。当背景溶液中离子强度(NaCl 浓度)从 0 增加至 10mmol/L 时,nTiO$_2$ 与金属离子之间的静电吸引会减弱,同时 Na^+与重金属离子竞争 nTiO$_2$ 表面吸附位点亦降低了 nTiO$_2$ 对重金属离子的吸附。③共存竞争性阴离子(如 Cl^-、NO_3^- 和 SO_4^{2-})会削弱磷酸盐对 nTiO$_2$ 吸附金属离子的增强作用,抑制顺序为:$SO_4^{2-}>NO_3^->Cl^-$,即与其离子半径的数量级成反比。这是由于共存阴离子与磷酸盐竞争 nTiO$_2$ 表面的吸附位点所致。研究结果表明,磷酸盐可以显著地增强 nTiO$_2$ 对重金属离子的去除效能,但是去除效能的大小会受到背景溶液中水化学条件的影响。

关键词: 纳米二氧化钛(nTiO$_2$); 重金属离子; 电感耦合等离子体发射光谱法; 磷酸盐; 阴离子; 吸附

要点:

(1) 磷酸盐的存在能有效地增强重金属在 nTiO$_2$ 上的吸附。
(2) 背景溶液中离子强度的增加会降低 nTiO$_2$ 对重金属离子的吸附效果。
(3) 共存竞争性阴离子会削弱磷酸盐对 nTiO$_2$ 吸附金属离子的增强作用。

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镉、锌、铬、铅和铜等重金属是废水中常见的污染物，它们在自然条件下不会降解成无害的产物[1]。重金属通过食物链等方式，能够在生物体中产生积累并对水生动物和人类造成直接或间接的有害影响[2-3]。例如，Cd^{2+}在人体内积累会导致骨质疏松、肾毒性和心血管疾病等[4]；Zn^{2+}中毒会导致电解质失衡、胃痛、恶心、脱水、肌肉不协调等症状[5]。因此，现阶段针对水体中重金属去除方法的研究引起了人们的广泛关注。吸附法由于具有成本低、效果好、材料易制备等优势[6-8]，已被广泛应用于去除废水中的重金属离子。该技术的研究关键在于研制成本低廉、高效的吸附剂。现在应用较多的吸附材料中，纳米金属氧化物（如纳米氧化锌、纳米二氧化钛和纳米氧化铈等）因其较大的比较面积和吸附特性被用于去除水体中的重金属离子[7-10]。其中，具有活化能高和表面积大的纳米二氧化钛（$n\mathrm{TiO_2}$），可以通过物理吸附和化学吸附等方式去除废水中的重金属离子[11-12]。王文凯等[13]利用TiO_2颗粒填充滤柱实现了对酸性废水中的高浓度砷进行连续在线吸附去除。聂晓等[14]以高指数晶面TiO_2为吸附剂，实现了对砷和锑的共吸附去除，其中As(Ⅲ)和Sb(Ⅴ)在TiO_2表面的最大吸附量分别为0.407mmol/g和0.181mmol/g。

迄今为止，人们对于不同环境条件下$n\mathrm{TiO_2}$对金属离子吸附开展了比较深入的研究[15-16]。研究结果表明，$n\mathrm{TiO_2}$对重金属离子的吸附行为受到吸附剂颗粒大小[17]、腐植酸[18]、pH[19]、固体浓度[20]和晶体结构[21]等多种物理化学因素的影响。聂晓等[14]研究发现TiO_2对Sb(Ⅲ)的吸附随着溶液pH的升高先增大后减小；而对As(Ⅴ)和Sb(Ⅴ)的吸附能力随pH升高逐渐降低。吴莉莉等[11]发现腐植酸表面丰富的基团可以与Cu^{2+}络合，促进TiO_2对Cu离子的吸附。考虑到水体环境的复杂性，需要更加全面地探究典型环境因子（如环境中普遍存在的无机配体）对TiO_2吸附重金属行为的影响。磷酸盐是水体环境中普遍存在的一种无机阴离子[22]。前期的研究表明磷酸盐能够通过氢键等作用与TiO_2纳米颗粒产生结合[23-24]，进而促进重金属离子在$n\mathrm{TiO_2}$上的吸附[25-26]。类似的，Xu等[22]发现，磷酸盐的加入显著促进了氧化锌纳米粒子对铅的吸附。然而，目前关于磷酸盐对$n\mathrm{TiO_2}$吸附金属离子影响的研究尚不完全，相关机制亦不清晰。

本文选取了Cd^{2+}和Zn^{2+}作为污染水体环境中典型的重金属离子，实验中采用$n\mathrm{TiO_2}$胶体颗粒对水体进行批量吸附，运用电感耦合等离子体发射光谱法（ICP-OES）测定滤液中的Cd^{2+}和Zn^{2+}浓度，探讨磷酸盐对重金属在$n\mathrm{TiO_2}$上的吸附特征的影响规律。同时探究不同水化学条件下（离子强度和共存阴离子），磷酸盐对$n\mathrm{TiO_2}$吸附重金属离子特性的影响。进一步采用经典吸附等温线模型对实验数据进行拟合，深入讨论相关吸附机制，为评估磷酸盐对$n\mathrm{TiO_2}$去除水体环境中重金属离子效果的影响提供数据支撑和理论依据。

1 实验部分

1.1 仪器和主要试剂

采用电感耦合等离子体发射光谱仪（iCAP 7000 SERIES，美国ThermoFisher公司，USA）测定实验体系中重金属的浓度；运用紫外可见分光光度计（TU-1810，北京普析通用仪器有限公司）测定$n\mathrm{TiO_2}$储备液的浓度。

恒温振荡器（TS-2012，常州国语仪器制造有限公司），电热鼓风干燥箱（101A-1E，上海实验仪器有限公司），离心机（L-530，湖南长沙湘仪检测设备有限公司），电子天平（BS124S，赛多利斯科学仪器有限公司）；pH计（PHS-3E，上海雷磁仪器有限公司），Zeta电位和粒径激光粒度仪（Nano-ZS90，Malvern，英国）。

本实验采用去离子水配制溶液。

1.2 实验材料

纳米TiO_2（$n\mathrm{TiO_2}$，纯度>99.9%）粉末购自阿拉丁生化科技（上海）公司。磷酸二氢钠、氯化镉（$CdCl_2$纯度>99.9%）、氯化锌（$ZnCl_2$，纯度>99.9%）：购自国药控股（上海）化学试剂有限公司。

1.3 实验方法

1.3.1 $n\mathrm{TiO_2}$悬浮液的制备与表征

实验所用$n\mathrm{TiO_2}$悬浮液是参考文献[27]方法制备：在1L去离子水中加入2g的$n\mathrm{TiO_2}$粉末，剧烈搅拌24h后静置10天。收集上部悬浮液作为后续实验所用的$n\mathrm{TiO_2}$悬浮液。

采用5mL硫酸-硫酸铵溶液消化后[28]，通过ICP-OES测定Zn^{2+}或Cd^{2+}的浓度。本研究中的$n\mathrm{TiO_2}$悬浮液浓度约为45mg/L。$n\mathrm{TiO_2}$的ζ-电位和水动力学直径（D_h）用Zeta电位和粒径激光粒度仪测定。

1.3.2 $n\mathrm{TiO_2}$胶体颗粒对重金属离子的吸附实验

在25±1℃室温下，将20mg/L的上述$n\mathrm{TiO_2}$悬

浮液样品、磷酸盐(0.1mmol/L NaH_2PO_4)和不同浓度的 Zn^{2+} 或 Cd^{2+}(0~15mg/L)加入 20mL 琥珀色玻璃小瓶中。用 0.1mol/L 盐酸和 0.1mol/L 氢氧化钠将溶液的 pH 值调整至 7.0。密封玻璃瓶后置于恒温振荡器上 150r/min 振荡 24h[29]。平衡后取下玻璃瓶,置于离心机内以 15000r/min 的速度离心 30min。取上清液过 0.22μm 孔径的滤膜,用 ICP-OES 测定滤液中 Zn^{2+} 或 Cd^{2+} 的浓度。

采用上述方法,本文研究了不同离子强度(1~20mmol/L 氯化钠)和共存竞争性阴离子(Cl^-、NO_3^- 和 SO_4^{2-})等条件下,磷酸盐对 nTiO$_2$ 吸附重金属的影响。

1.4 数据处理

吸附在 nTiO$_2$ 胶体上的重金属的质量按照下述公式来计算。为保证数据质量,每组实验重复 3 次。

$$q=\frac{(C_0-C_e)V}{m} \tag{1}$$

式中:q 是吸附容量(mg/g);C_0 是重金属离子的初始浓度(mg/L);C_e 是重金属离子的平衡浓度(mg/L),V 是溶液的体积(L);m 是 nTiO$_2$ 胶体的质量(g)。

重金属的等温吸附过程利用 Freundlich 方程(式 2)和 Langmuir 方程(式 3)进行吸附等温线的模型拟合:

$$q=K_F C_e^n \tag{2}$$

$$q=\frac{q_{max}K_L C_e}{1+K_L C_e} \tag{3}$$

式中:q 为吸附平衡时单位吸附剂吸附的物质质量(mg/g);K_F 为 Freundlich 吸附常数($mg^{1-n}\cdot L^n/g$),反映吸附剂吸附能力大小;n 为常数。q_{max} 为最大吸附量(mg/g);K_L 为 Langmuir 吸附常数,表示吸附亲和力(L/g);C_e 为吸附平衡时重金属的浓度(mg/L)。

2 结果与讨论

2.1 磷酸盐浓度对 nTiO$_2$ 吸附 Zn^{2+} 和 Cd^{2+} 的影响

不同的磷酸盐浓度对 nTiO$_2$ 对 Zn^{2+} 和 Cd^{2+} 的吸附影响显著。本文实验结果(表 1)显示,磷酸盐的加入增强了 nTiO$_2$ 对 Zn^{2+} 和 Cd^{2+} 的吸附。在 pH 7.0、背景电解质 1.0mmol/L NaCl 条件下,无磷酸盐时,nTiO$_2$ 对 Zn^{2+} 和 Cd^{2+} 的最大吸附量分别为 121.1mg/g 和 84.7mg/g;而加入 0.5mmol/L 磷酸盐后,nTiO$_2$ 对 Zn^{2+} 和 Cd^{2+} 的最大吸附量分别为 588.3mg/g 和 434.8mg/g,相比不加磷酸盐增加了 3.8~4.1 倍。

磷酸盐促进了 nTiO$_2$ 对 Zn^{2+} 和 Cd^{2+} 吸附,其主要原因分析如下:①随着水相中磷酸盐浓度的增加,nTiO$_2$ 的表面 Zeta 电位变得更负(图 1),此时带负电荷的纳米颗粒与带正电荷的金属离子之间的静电引力会随磷酸盐含量的增加而增大。②随着磷酸盐浓度的增加,nTiO$_2$ 水动力学直径减小(图 1),这表明磷酸盐的加入抑制了 nTiO$_2$ 纳米颗粒的聚集,增加了吸附位点,金属离子可以与更多的 nTiO$_2$ 颗粒充分地接触。③磷酸盐可以在 nTiO$_2$ 表面形成内球表面复合物,从而极大地影响纳米颗粒的表面化学性质[23-24]。因此,磷酸盐能够通过桥连作用与 nTiO$_2$ 和重金属形成金属-磷酸盐-nTiO$_2$ 三元复合物,从而增强了 nTiO$_2$ 对金属离子的吸附。类似的,Wang 等[30]研究发现了磷酸盐通过与针铁矿形成表面单齿配合物,导致此类矿物对 Cd^{2+} 吸附量的增加。

此外,在相同的实验条件下,nTiO$_2$ 对 Zn^{2+} 的吸附量大于对 Cd^{2+} 的吸附量,这可能与金属离子的化学特性如离子半径和水解常数(pK_h)有关。

由以上分析可知,静电作用是吸附过程中的一

表 1 nTiO$_2$ 吸附 Zn^{2+} 和 Cd^{2+} 的 Langmuir 和 Freundlich 模型动力学参数

Table 1 Kinetic parameters for the Langmuir and Freundlich models of Zn^{2+} and Cd^{2+} adsorption onto nTiO$_2$

实验序号	金属离子	背景电解质	磷酸盐浓度	Langmuir 模型			Freundlich 模型		
			(mmol/L)	K_L(L/mg)	q_{max}(mg/g)	R^2	K_F($mg^{1-n}L^n/g$)	n	R^2
1	Zn^{2+}	1mmol/L NaCl	0	1.07	121.1	0.993	53.3	0.447	0.975
2	Zn^{2+}	1mmol/L NaCl	0.1	0.375	476.2	0.998	110.3	0.742	0.980
3	Zn^{2+}	1mmol/L NaCl	0.5	0.894	588.3	0.981	211.8	0.636	0.972
4	Cd^{2+}	1mmol/L NaCl	0	2.745	84.7	0.971	37.3	0.596	0.981
5	Cd^{2+}	1mmol/L NaCl	0.1	0.884	263.2	0.980	61.6	0.673	0.984
6	Cd^{2+}	1mmol/L NaCl	0.5	0.535	434.8	0.993	85.1	0.777	0.983

个重要机制。与 Cd^{2+} 的离子半径(0.097nm)相比，Zn^{2+} 的离子半径(0.074nm)更小，说明前者离子的静电效应更强[31]。另外，Zn^{2+} 和 Cd^{2+} 的第一水解常数分别为 9.0 和 10.1[32]。一般来讲，具有较低水解常数的金属离子对交换位点的静电吸引更高[33]。

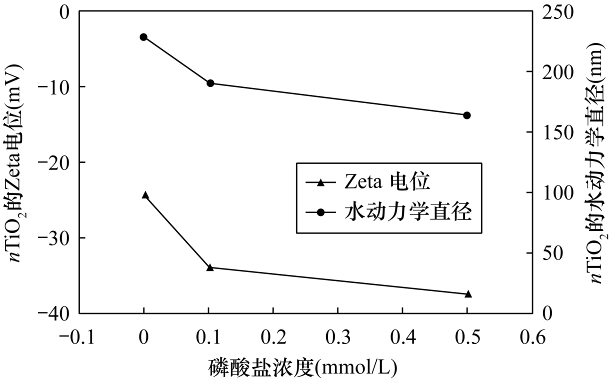

图 1 磷酸盐对 $nTiO_2$(20mg/L，pH 7.0)的 Zeta 电位和水动力学直径的影响

Fig. 1 The ζ-potential and hydrodynamic diameter of $nTiO_2$ (20mg/L at pH 7.0) decreased with the increasing of phosphate concentration from 0 to 0.5mmol/L.

2.2 背景溶液中不同离子强度条件下磷酸盐对 $nTiO_2$ 吸附重金属的影响

磷酸盐对 $nTiO_2$ 吸附重金属受到背景溶液中离子强度的影响。本实验通过加入不同浓度的氯化钠，来探究不同离子强度条件下磷酸盐对 $nTiO_2$ 吸附重金属的影响。结果如图 2 所示，当背景电解质氯化钠的浓度从 0mmol/L 增加到 10mmol/L 时，$nTiO_2$ 对 Zn^{2+} 和 Cd^{2+} 的 K_d 值（固液分配系数，$K_d = q/C_e$）分别从 285.3L/g 和 202.5L/g 下降到 36.6L/g 和 31.6L/g。离子强度可能通过以下三种主要机制影响吸附行为：第一，竞争阳离子(Na^+)的存在降低了 $nTiO_2$ 对金属离子(Zn^{2+} 和 Cd^{2+})的吸附；且随着 Na^+ 浓度的增加，这种作用更为显著[34]。第二，如图 3 所示，随着离子强度的增加，$nTiO_2$ 的 Zeta 电位变得越来越正，从而减弱了 $nTiO_2$ 与金属离子之间的静电引力。第三，离子强度的增加显著地增强了 $nTiO_2$ 颗粒的团聚特征(图 3 所示)，降低了 $nTiO_2$ 的表面活性位点，从而抑制了 $nTiO_2$ 对重金属离子的吸附。

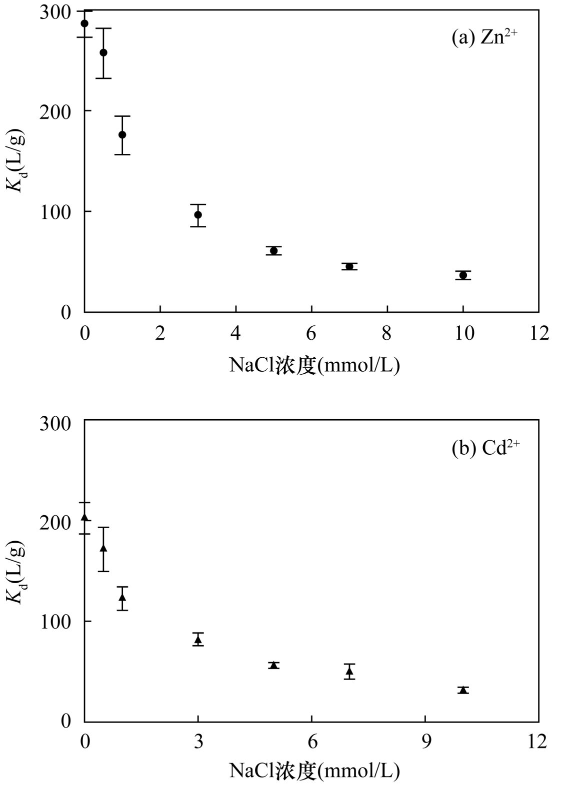

图 2 在 0.1mmg/L 磷酸盐存在下，离子强度对(a) Zn^{2+} 和(b) Cd^{2+} 吸附分配系数(K_d)的影响情况

Fig. 2 Effect of ionic strength (NaCl) on distribution coefficient (K_d) for adsorption in the presence of 0.1mmol/L phosphate at equilibrium pH of approximately 7.0: (a) Zn^{2+} and (b) Cd^{2+}, K_d decreased with the increasing of ionic strength (NaCl) from 0 to 10 mmol/L.

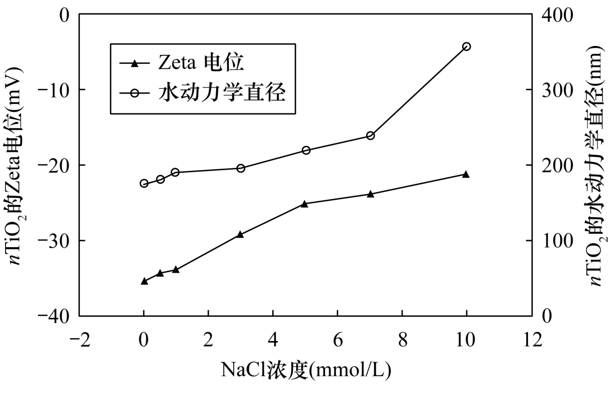

图 3 在磷酸盐存在条件下，离子强度对 $nTiO_2$(pH 7.0)的 Zeta 电位和水动力直径的影响情况

Fig. 3 Effects of ionic strength on the Zeta potential and hydrodynamic diameter of $nTiO_2$ (pH 7.0) in the presence of phosphate.

2.3　竞争阴离子存在条件下磷酸盐对 $n\mathrm{TiO_2}$ 吸附重金属的影响

考虑到磷酸盐极可能与多种阴离子共存于天然废水系统中，研究表明共存阴离子（如硝酸盐和硫酸盐）也能够与 $n\mathrm{TiO_2}$ 产生相互作用[35]，进而影响磷酸盐对 $n\mathrm{TiO_2}$ 吸附重金属的增强作用。基于此，本文研究了在竞争阴离子存在时，磷酸盐对 $\mathrm{Zn^{2+}}$ 和 $\mathrm{Cd^{2+}}$ 吸附的影响。图 4 结果表明，添加竞争阴离子后，磷酸盐对金属离子吸附的影响略有所降低。在无竞争阴离子的情况下，$\mathrm{Zn^{2+}}$ 的最大吸附量（$q_{\max}$）为 485.7mg/g，但在 1mmol/L $\mathrm{SO_4^{2-}}$ 的存在情况下，$\mathrm{Zn^{2+}}$ 的 $q_{\max}$ 值降至 434.6mg/g。这是由于这些阴离子与磷酸盐竞争 $n\mathrm{TiO_2}$ 表面的吸附位点[36-37]，从而削弱了磷酸盐对纳米颗粒吸附 $\mathrm{Zn^{2+}}$ 和 $\mathrm{Cd^{2+}}$ 的增强作用。

此外，竞争性阴离子对磷酸盐促进重金属在上 $n\mathrm{TiO_2}$ 吸附行为的抑制效果与离子种类有关，且对抑制效果的大小顺序为：$\mathrm{SO_4^{2-}}>\mathrm{NO_3^-}>\mathrm{Cl^-}$。如图 5 所示，在 $\mathrm{Cl^-}$、$\mathrm{NO_3^-}$ 和 $\mathrm{SO_4^{2-}}$ 存在条件下，$\mathrm{Zn^{2+}}$ 的 $q_{\max}$ 分别为 476.2mg/g、454.1mg/g 和 434.6mg/g。值得注意的是，抑制作用的顺序与其离子半径的数量级成反比[36-37]。一方面是具有较高离子半径的阴离子（如 $\mathrm{SO_4^{2-}}$）能够占据更多的 $n\mathrm{TiO_2}$ 表面活性位点；另一方面是竞争性吸附也与阴离子的价态有关，一价阴离子和重金属离子的静电作用力比二价阴离子要弱[38]。因此，$\mathrm{Cl^-}$ 和 $\mathrm{NO_3^-}$ 在金属离子吸附过程中与磷酸盐竞争吸附的影响要小于 $\mathrm{SO_4^{2-}}$。

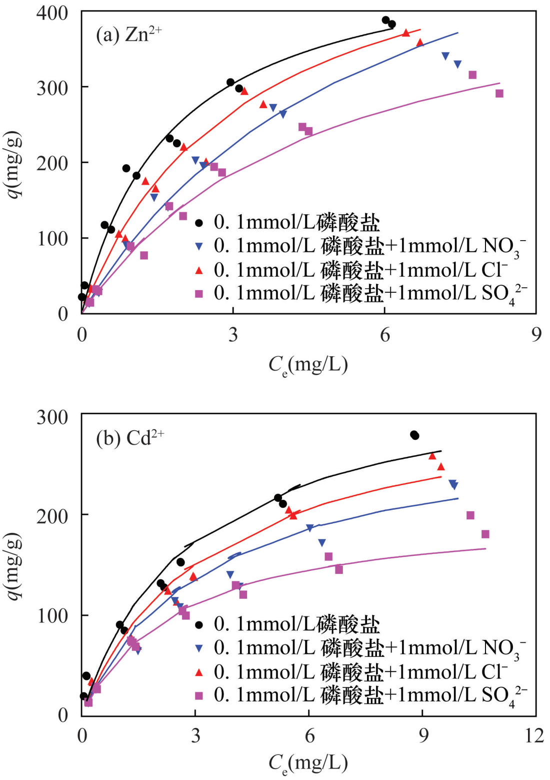

图 4　**竞争性阴离子存在情况下，磷酸盐（0.1mmol/L）对 $n\mathrm{TiO_2}$ 吸附（a）$\mathrm{Zn^{2+}}$ 和（b）$\mathrm{Cd^{2+}}$ 金属离子的影响（虚线是 Langmuir 模型拟合结果）**

Fig. 4　Effects of phosphate (0.1mmol/L) on adsorption of metal ions onto $n\mathrm{TiO_2}$ in the presence of competitive anions: (a) $\mathrm{Zn^{2+}}$ and (b) $\mathrm{Cd^{2+}}$. The dashed lines on the panel are the Langmuir model fitting results.

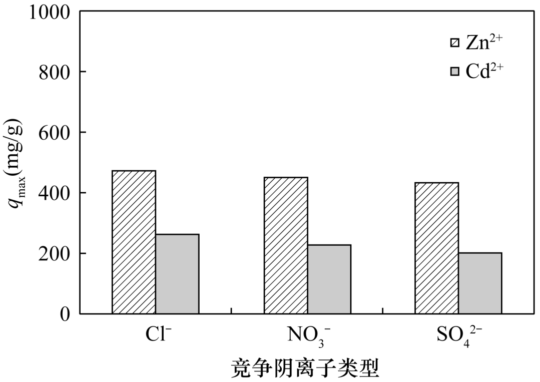

图 5　**磷酸盐（0.1mmol/L）对 $\mathrm{Zn^{2+}}$ 和 $\mathrm{Cd^{2+}}$ 在 $n\mathrm{TiO_2}$ 上最大吸附量（$q_{\max}$）受竞争性阴离子的影响情况**

Fig. 5　Effects of phosphate (0.1mmol/L) on the $q_{\max}$ values of $\mathrm{Zn^{2+}}$ and $\mathrm{Cd^{2+}}$ by $n\mathrm{TiO_2}$. The coexistence of competitive anions (such as $\mathrm{Cl^-}$, $\mathrm{NO_3^-}$ and $\mathrm{SO_4^{2-}}$) will weaken the enhancement effect of phosphate (0.1mmol/L) on the adsorption of metal ions on $n\mathrm{TiO_2}$, and the order of inhibition is: $\mathrm{SO_4^{2-}}>\mathrm{NO_3^-}>\mathrm{Cl^-}$.

3　结论

通过研究得出如下结论：①磷酸盐能够通过桥连作用形成金属-磷酸盐-$n\mathrm{TiO_2}$ 三元络合物，以及增加了重金属离子和胶体颗粒之间的静电引力，显著地增强了 $n\mathrm{TiO_2}$ 对重金属离子的吸附。②背景溶液中氯化钠的加入减弱了 $n\mathrm{TiO_2}$ 对金属离子的静电吸引，同时 $\mathrm{Na^+}$ 与重金属离子竞争吸附位点，从而降低了 $n\mathrm{TiO_2}$ 对重金属离子的吸附效果。③竞争性阴离子的加入削弱了磷酸盐对 $n\mathrm{TiO_2}$ 吸附金属离子的增强作用，其抑制顺序为：$\mathrm{SO_4^{2-}}>\mathrm{NO_3^-}>\mathrm{Cl^-}$。

综上所述，磷酸盐可显著地增强 $n\mathrm{TiO_2}$ 对重金属离子的吸附，但增强效果受制于背景溶液中的水化学条件，故 $n\mathrm{TiO_2}$ 应用于修复重金属污染水体时，需要充分考虑污染水体的实际情况。鉴于目前水体中呈现多种重金属复合污染的态势，对于不同重金

属共存时，磷酸盐对多种重金属离子在 $n\mathrm{TiO_2}$ 上竞争吸附的影响规律还有待进一步研究。此外，实际环境水体中的成分非常复杂，通常含有天然有机质、表面活性剂、共存天然胶体颗粒等成分，这些成分对磷酸盐存在条件下 $n\mathrm{TiO_2}$ 对重金属离子的去除效果有何影响，还需要进一步开展全面研究。

Effects of Phosphate on the Adsorption of Heavy Metal Ions onto $\mathrm{TiO_2}$ Nanoparticles in Water and Mechanism Analysis

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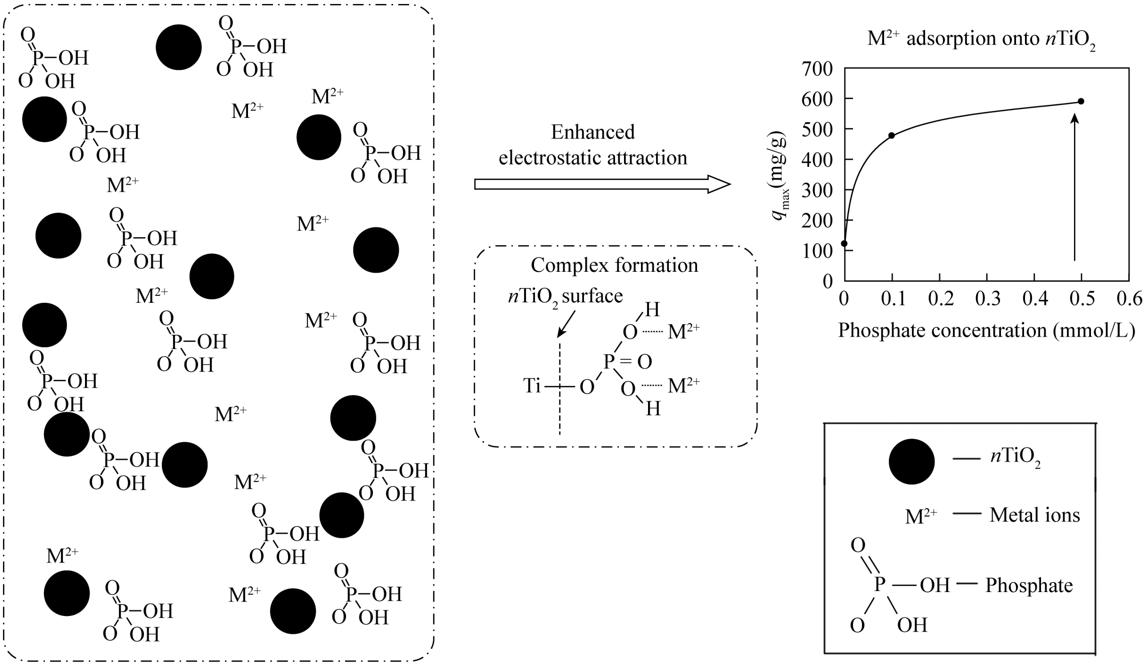
HIGHLIGHTS

(1) The presence of phosphate enhances the adsorption of metal ions onto $n\mathrm{TiO_2}$.

(2) Increased ionic strength decreases the adsorption effect of the heavy metal ions onto $n\mathrm{TiO_2}$.

(3) Coexistence of competing anions will weaken the enhancement effect of phosphate on the adsorption of metal ions onto $n\mathrm{TiO_2}$.



ABSTRACT

BACKGROUND: Nano-titanium dioxide (*n*TiO_2) is widely used to remove heavy metals from water. Phosphate, a common inorganic anion in the aquatic environment, can affect the adsorption characteristics of heavy metal ions on *n*TiO_2. However, the current state of knowledge on the influences of phosphate on the adsorption behaviors of heavy metal ions onto TiO_2 nanoparticles (*n*TiO_2) is inadequate. Herein, batch adsorption experiments were conducted to investigate the effects of phosphate on the adsorption of heavy metal ions (i. e. , Zn^{2+} and Cd^{2+}) onto suspended *n*TiO_2.

OBJECTIVES: To elucidate the primary mechanisms controlling the adsorption behaviors of Zn^{2+} and Cd^{2+} on suspended *n*TiO_2 in the presence of phosphate under different solution chemistry conditions.

METHODS: In order to determine the effects of phosphate on the adsorption of heavy metal ions onto *n*TiO_2, batch experiments were conducted by mixing background electrolyte ions, *n*TiO_2, and phosphate, which contained various concentrations of Zn^{2+} or Cd^{2+} in 20mL-amber glass vials at room temperature. The pH of solution was adjusted to target 7. 0 using 0. 1mol/L HCl or 0. 1mol/L NaOH accordingly. Then, the mixtures were rotated end-over-end for 24h. After equilibration, the liquid and solid phases were separated by centrifugation at 15000r/min for 20min, and then the supernatants were filtered through 0. 22μm pore-size cellulose ester membrane filter (the loss of metal ions can be neglected). The concentrations of Zn^{2+} or Cd^{2+} in the filtrate were measured by an inductively coupled plasma-optical emission spectrometry (ICP-OES). The adsorbed metal ions were then determined by the difference between the initial and final concentrations of metal ions in the aqueous phase. Furthermore, the classic Langmuir and Freundlich sorption models were used to correlate the adsorption isotherms.

RESULTS: (1) Adsorption isotherms showed that the presence of phosphate could enhance the adsorption of metal ions onto *n*TiO_2, the maximum adsorption capacity of Zn^{2+} and Cd^{2+} increased from 121. 1mg/g and 84. 7mg/g to 588. 3mg/g and 434. 8mg/g, respectively. We propose that phosphate probably enhance the adsorption of Zn^{2+} and Cd^{2+} onto *n*TiO_2 by the following mechanisms. Firstly, the ζ-potential of *n*TiO_2 surface becomes more negative with the increase of phosphate concentration in aqueous phase. Consequently, the electrostatic attraction between negatively charged nanoparticles and positively charged metal ions generally increases with increasing phosphate content. Secondly, the phosphate added into *n*TiO_2 suspension inhibits the aggregation of nanoparticles. In this case, more *n*TiO_2 could sufficiently contact metal ions, thus increasing the adsorption sites. Thirdly, phosphate could form an inner-sphere surface complex on the *n*TiO_2 surface, which can greatly influence the surface chemistry of *n*TiO_2[55-57]. These products could strongly immobilize heavy metal ions[40-41]. These results might account for enhanced Zn^{2+} and Cd^{2+} adsorption on *n*TiO_2 by forming metal-phosphate-surface ternary complexes in the presence of phosphate.

(2) The adsorption of heavy metals onto *n*TiO_2 decreased when concentration of NaCl increased from 0 to 10 mmol/L. It is likely that ionic strength can affect the attachment of nanoparticles *via* three major mechanisms. Firstly, the presence of competing cations (Na^+) of salt reduces the adsorption of metal ions (i. e. , Zn^{2+} and Cd^{2+}) and this effect may have more significant roles with increasing Na^+ concentration. Secondly, this could be related to the fact that an increase in ionic strength interferes with the electrostatic attraction between *n*TiO_2 and metal ions. Thus, adsorption of metal ions is suppressed. Thirdly, increasing ionic strength significantly enhances aggregation of *n*TiO_2, and consequently decreases the active surface sites of *n*TiO_2.

(3) The coexistence of competing anions (such as Cl^-, NO_3^- and SO_4^{2-}) weaken the enhancement effect of phosphate on the adsorption of metal ions onto *n*TiO_2, and the order of inhibition is: $SO_4^{2-}>NO_3^->Cl^-$. This may be because anions with higher ionic radii (i. e. , SO_4^{2-}) may occupy more surface reactive sites. On the other hand, the competitive adsorption is related to the valence. It is well known that Cl^- and NO_3^- are more likely to form “outer sphere” complexes with binding surfaces. Meanwhile, the electrostatic adsorption and the ion energy of monovalent anions (e. g. , Cl^- and NO_3^-) are weaker than those of divalent anions (e. g. , SO_4^{2-}). For this reason, the competitive influence of Cl^- and NO_3^- during the adsorption of metal ions is negligible. In comparison, the divalent anion has a relatively stronger competitiveness on the adsorption of metal ions.

CONCLUSIONS: The research results show that phosphate can significantly enhance the removal efficiency of $n\mathrm{TiO_2}$ to heavy metal ions, but the removal efficiency will be affected by the water chemical conditions in the background solution. Previous studies show that $n\mathrm{TiO_2}$ is promising as an adsorbent for the removal of metal ions from aqueous solution. The present study demonstrates that phosphate plays an important role in adsorption of metal ions (e.g., $\mathrm{Zn^{2+}}$ and $\mathrm{Cd^{2+}}$) onto $n\mathrm{TiO_2}$. Phosphate significantly enhances adsorption of $\mathrm{Zn^{2+}}$ and $\mathrm{Cd^{2+}}$ onto $n\mathrm{TiO_2}$ by forming metal-phosphate-surface ternary complexes and increasing electrostatic attraction. The increase of ionic strength results in the low adsorption of metal ions in the presence of phosphate, resulting from electronic shielding of the negatively charged sites on the $n\mathrm{TiO_2}$ surface and competition between $\mathrm{Na^+}$ and heavy metal ions for active surface sites. Moreover, the addition of competitive anions inhibits the adsorption of metal ions in the presence of phosphate following the order of $\mathrm{SO_4^{2-}} > \mathrm{NO_3^-} > \mathrm{Cl^-}$. This phenomenon is mainly ascribed to the decrease of phosphate adsorption because of competition between anions and phosphate for adsorption sites on $n\mathrm{TiO_2}$ surface, resulting in decreasing the amount of metal-phosphate-surface ternary complexes. Overall, the results obtained from this study indicate that the adsorption of metal ions onto $n\mathrm{TiO_2}$ varies greatly with factors such as phosphate, ionic strength, and competitive anions. Therefore, these factors should be well considered to better understand the fate and toxicity of metal ions in the adsorption process for the treatment of wastewater.

KEY WORDS: nano-titanium dioxide ($n\mathrm{TiO_2}$); heavy metal ions; inductively coupled plasma-optical emmission spectrometry; phosphate; anions; adsorption

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