土壤性质对锌吸附影响的研究进展

张会民[1,2,3],吕家珑[1],徐明岗[2],刘红霞[3]

(1 西北农林科技大学 资源环境学院,陕西 杨凌 712100;
2 中国农业科学院 农业资源与农业区划研究所,北京 100081;
3 河南科技大学 农学院,河南 洛阳 471003)

[摘 要] 概括了土壤 pH、有机质、粘粒矿物、温度、竞争性阳离子和共存阴离子等性质对土壤锌吸附过程的影响,总结了土壤对锌的吸附量随 pH 值、有机质含量、粘粒矿物类型、温度和土壤溶液中伴随离子种类变化而变化的机理,指出了土壤性质对锌吸附影响研究中存在的问题及今后的研究方向。

[关键词] 土壤性质;锌吸附;重金属污染;污染修复
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尽管锌是植物必需的营养元素,但是由于污水、污泥等工业和城市废物的大量排放及锌肥的不合理施用,都有可能造成锌在土壤中的积累,增加了农业生态污染的危险,从而对土壤、水质及农产品产量和品质产生不利的影响[1,2]。影响锌在土壤溶液中的浓度和生物有效性的因素有金属锌的浓度及化学性质、支持电解质的浓度及组成、土壤性质和环境条件等诸多因素,其中土壤性质如土壤 pH、有机质含量、土壤温度、土壤矿物类型和土壤溶液中的共存离子等均对吸附过程及机理有决定性的影响[3-6]。本文主要概述了土壤性质对锌吸附过程和吸附机理的影响,并对该领域今后的研究方向进行了展望,以期为重金属锌污染土壤的修复研究提供理论依据。

1 pH 对土壤锌吸附的影响

pH 可能会影响被吸附锌的形态,土壤锌吸附机理模型可简单描述为:

$$Zn^{2+} + S^{y-} = ZnS^{(2-y)+} \quad (1)$$

$$ZnOH^{+} + S^{y-} = ZnOHS^{(1-y)+} \quad (2)$$

式中,S 代表表面吸附点位;y 表示表面吸附点位电荷。式(1)的进行将抑制 Zn^{2+} 的水解而使溶液 pH 升高,式(2)的进行将促进 Zn^{2+} 的水解而使溶液 pH 降低[7]。

Masky 等[8]研究了 pH 对褐色淤泥土、氧化土和灰化土铜锌吸附的影响,结果表明,pH 可能会影响锌的羟基化形态或吸附表面对锌的亲和能力,从而影响锌的吸附量。概括起来,pH 可能通过影响锌形态的变化[7]、与 $(H_2O)^{+}$ 和 Al^{3+} 竞争负电荷点位[8]、表面基团的离子化[9]、表面交换反应平衡[10-11]等方式影响锌的吸附过程。

不论是在酸性、中性还是在石灰性土壤中,锌的吸附量均随 pH 的增大而增加[3,12-14]。Pardo 等[13]研究了 pH 对西班牙两种酸性土壤锌吸附和解吸的影响,结果表明,随着 pH 增加,土壤吸附表面的负电荷增加,当 pH>6 时,增加迅速,此时锌的吸附量也呈现出相同的趋势。Gupta 等[14]研究了 pH 对印度碱性土壤锌吸附的影响,也得出了类似的结论。pH 与锌吸附等温线方程的参数密切相关,Karimian 等[15]研究了伊朗石灰性土壤锌的吸附特点,得出 pH 与吸附等温线方程参数间的相关关系为

$$A = -2.748 + 396 \times pH + 1.18 \times 粘粒含量$$

$$R^2 = 0.470 \quad (3)$$

$$K = -4.67 + 0.589 \times pH + 0.001\,57 \times 粘粒含量$$

$$R^2 = 0.410 \quad (4)$$

式中,A 是 Freundlich 方程的吸附系数;K 是与结合能有关的 Langmuir 方程的系数。由式(3)和式(4)可以看出,pH 通过影响吸附系数 A 及与结合能有关的参数 K 而影响锌的吸附量。

Chairidchai 等[7]的研究结果也表明,锌的吸附

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[作者简介] 张会民(1969-),男,河南宜阳人,副教授,博士,主要从事重金属污染土壤修复研究。E-mail:zhhm2007@163.com
[通讯作者] 徐明岗(1961-),男,陕西武功人,研究员,博士生导师,博士,主要从事土壤污染生态环境的修复研究。E-mail:mgxu@caas.ac.cn

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量随 pH 增加而增加，但与上述结论不同的是，随着 pH 的变化，锌吸附量变化幅度不大，他们认为这可能是由于试验中所用锌的浓度和支持电解质浓度不同所致，他们所用锌的浓度较低，更接近农业土壤中锌的实际浓度。而上述研究者们所用锌的浓度均较高，在非污染土壤上一般不存在这种情况。

2　有机质对土壤锌吸附的影响

土壤有机质是吸持重金属最主要的土壤组分之一[16]。大量研究[4,17-18]表明，土壤锌的吸附量随土壤有机质含量的增加而增大，反之，如果土壤有机质含量降低则锌的吸附量也随之减少。Yuan 等[17]的研究结果表明，当土壤有机质含量从 46.0 g/kg 降低到 40.9 g/kg 时，土壤锌的吸附量下降了 28%。

对质地不同的土壤，有机质对土壤锌吸附的影响也不同。Shuman[19]的研究表明，施用工业有机污泥和腐殖酸增加了土壤锌的吸附量，其中对砂质土的影响较粘质土显著，如果工业污泥中含有较多的水溶性炭，则导致土壤锌的吸附量降低。Polo 等[20]研究了西班牙南部石灰性土壤施用工业污泥对铜锌吸附的影响，结果表明，虽然施入的工业污泥有机质含量很高，但土壤锌的吸附量降低。究其原因可能是由于供试土壤对锌的吸附机理主要涉及阳离子交换点位(CEC)所致。

3　土壤矿物对土壤锌吸附的影响

土壤矿物种类不同，其表面功能团的类型和活性也有差异。对于 2∶1 型蛭石、蒙皂石和伊利石等矿物而言，其表面功能团主要是硅氧烷复三角网孔功能团；而对 1∶1 型高岭石类矿物而言，其表面功能团主要是铝醇基、Lewis 酸点位和硅烷醇基；土壤粘粒氧化物、氢氧化物、水铝英石类的边缘断键处的表面功能团均为羟基[21]。不同类型的土壤矿物对锌的吸附能力及吸附机理不同。Abd-Elfattah 等[22]的研究表明，以 Ca^{2+} 作为参考离子，不同矿物对 Zn^{2+} 的选择性吸附顺序为：蒙脱石 ＜高岭石 ＜ 水铝英石 ＜ 氧化铁。在多数自然体系中，Zn^{2+} 能和土壤中的铁、铝、锰氧化物和粘土矿物形成各种络合物[23-25]。晶形氧化物(如针铁矿)较非晶形氧化物具有更高的吸附能[26]，所以 Zn^{2+} 和非晶形铁锰氧化物主要形成外层络合物[27]，而 Zn^{2+} 与晶形氧化物(如针铁矿)、亚稳性铁氧化物(如水铁矿)及其他晶形矿物(如方解石)等主要形成内层络合物[27-28]。

4　共存离子对土壤锌吸附的影响

4.1　共存阳离子

不同的土壤或土壤组分对不同金属离子的吸附能力不同。对 Zn^{2+} 而言，如果土壤溶液中与其共存的其他金属阳离子被土壤吸附的能力强，那么土壤对 Zn^{2+} 的吸附量就可能减少[29]。不同研究者得到的不同土壤或土壤组分对锌等金属离子的吸附亲和次序如表 1 所示。

表 1　不同类型土壤或土壤组分对不同金属元素的吸附亲和次序

Table 1　Affinity sequences of absorption of metals by soils and soil componets

土壤或土壤组分 Soils or soil components	亲和次序 Affinity sequences	参考文献 Reference
泥炭土 Peat soil	Pb＞Cu＞Cd＝Zn＞Ca	Bunzl 等[30]
针铁矿 Goethite	Cu＞Pb＞Zn＞Cd	Forbes 等[31]
铁氧化物 Ferric oxide	Pb＞Cu＞Zn＞Cd	Kinniburgh 等[32]
不同 CEC 物质 Different CEC materials	Pb＝Cu＞Zn＞Cd＞Ca，Mg	Abd-Elfattah 等[22]
土壤 Soil	Cu≫Zn≥Ni≥Pb	Tyler 等[33]
铁氧化物粘土 Ferric oxide clay	Zn＞Ni＞Cd	Tiller 等[34]
硅酸盐粘土 Silicate clay	Zn≫Ni＝Cd	Tiller 等[34]
土壤 Soil	Pb＞Cu＞Zn＞Cd	Elliott 等[35]
针铁矿 Goethite	Cu＞Pb＞Zn＞Cd＞Co＞Ni＞Mn	Schwertmann 等[36]
赤铁矿 Hematite	Pb＞Cu＞Zn＞Cd＞Co＞Ni＞Mn	Schwertmann 等[36]
土壤 Soil	Pb＞Cu＞Ni≥Cd＝Zn	Basta 等[1]
土壤 Soil	Cr＞Pb＞Cu＞Cd＞Zn＞Ni，Pb＞Cr＞Cu＞Cd＞Ni＞Zn	Gomes 等[37]
土壤 Soil	Cr～Pb≫Cu≫Ni＞Cd ～Zn	Fontes 等[38]

此外，支持电解质中共存的阳离子可能通过直接与锌竞争吸附点位和影响双扩散层化学性质而影响锌的吸附[39]。Bowden 等[40]报道，土壤吸附表面电位与离子化合价有关，这可能是离子化合价影响土壤表面电荷密度所致。在 pH 大于零净电荷点(PZNC)的情况下，阳离子化合价增加使土壤吸附

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表面负电荷减少,所以阳离子的吸附量也随之降低。在吸附研究[41-42]中最常用的指示阳离子除 Ca^{2+} 和 Na^+ 外,还有 Mg^{2+} 和 K^+,其中 Ca^{2+} 对锌吸附的抑制作用可能最强,其次是 Mg^{2+},K^+ 和 Na^+。此外,抑制程度还取决于与这些阳离子相伴的阴离子种类和溶液 pH 以及土壤类型等因素[43-44]。

4.2 共存阴离子

土壤溶液中阴离子,如 SO_4^{2-},HPO_4^{2-},$H_2PO_4^-$,Cl^- 和 NO_3^- 等的存在也会影响锌的吸附[45-47]。大量研究[45,47-48]表明,磷酸盐的存在可能会促进或抑制锌的吸附,也可能对锌的吸附无影响,如 Barrow[45] 认为,锌和磷酸盐被吸附在相反电荷的表面点位上,磷酸盐通过影响溶液 pH 和/或吸附表面电荷,通过升高或降低 pH 而导致锌吸附量的增加或降低。Shuman[49]的研究表明,当溶液中(pH=6)共存阴离子为 SO_4^{2-} 时,锌的吸附量较溶液中共存阴离子为 Cl^- 和 NO_3^- 时高,这是由于土壤吸附 SO_4^{2-} 后引起吸附表面电位的变化所致[50]。此外还可能与 Cl^- 和 NO_3^- 是非专性吸附,所以锌的吸附量小,而 SO_4^{2-} 是专性吸附,故锌的吸附量大有关[51]。Padmanabham[52]在研究针铁矿对锌的吸附时发现,当 Cl^- 存在时锌的吸附量较 NO^{3-} 存在时高,究其原因,可能是由于在低 pH(4.0~4.5)时,Cl^- 似乎和 Zn^{2+} 形成了更牢固的络合物从而促进了锌的吸附。但当 pH>6 时,Cl^- 和 NO_3^- 对锌吸附的影响差异较小。Elrashidi 等[53]发现,当 SO_4^{2-},Cl^- 和 NO_3^- 与锌共存时,这些阴离子对砂质壤土(pH=7.6)锌吸附的影响差异不显著。

5 土壤温度对土壤锌吸附的影响

土壤温度的日变化和年变化对锌的吸附过程和吸附量有显著影响。Aharoni 等[54]依据热动力学原理进行的研究表明,金属离子吸附量随土壤温度的升高而增加。通过研究温度和时间对锌吸附的影响,可以预测进入土壤的锌在不同温度和不同时期的毒效,有学者[55-56]用改进的 Freundlich 方程来描述时间和温度对锌吸附的影响,其结果为

$$S = ac^{b_1}(A^{(-E/RT)}t)^{b_2} \quad (5)$$

式中,S 为吸附量(μmol/g);c 为溶液中锌的零点(null-point)浓度(μmol/L);b_1 为 Freundlich 吸附曲线的斜率;E 为活化能(kJ/mol);R 为气体常数;T 为温度(K);t 为培养时间(d);a 和 b_2 为系数。Barrow[55]的研究结果表明,b_1 值为 0.582。

6 结语与展望

土壤是整个地球生态系统的重要组成部分,是由固相、液相和气相组成的复杂的非均质体系。锌是植物必需的微量元素,但由于自然或人类活动的影响,可能造成其在土壤中的过量积累,从而影响农产品的产量和质量,甚至通过食物链危害人畜健康。吸附作用是决定锌在土壤中积累的重要作用之一,吸附过程和机理受多方面因素的影响,其中土壤性质对土壤锌吸附起决定性作用。土壤有机质和土壤矿物是土壤锌的重要吸附剂,它们表面不同类型的功能团能显著影响锌的吸附过程及机理;竞争性阳离子的存在抑制锌的吸附,土壤溶液中共存阴离子是促进还是抑制锌的吸附,则取决于阴离子的种类和土壤的类型。

pH 是影响土壤锌吸附过程及机理的最重要的土壤性质之一。不论是土壤有机质和土壤矿物,还是共存阴离子和阳离子,对土壤锌吸附的影响程度及具体作用过程均与 pH 密切相关。

土壤锌吸附量随 pH 增加而增大,主要原因包括:pH 影响吸附表面电荷、影响被吸附锌的形态和(或)影响吸附表面对锌的亲和力,目前对后两者的界定还存在分歧,在锌的吸附过程中,究竟是被吸附锌形态的影响、还是吸附表面亲和力的影响占主导地位,尚需进一步研究。目前,在 pH 对土壤锌吸附的影响研究中,大多采用的锌浓度较高(除污染土壤外一般土壤不存在这样高的浓度范围),而采用更接近于农业土壤实际锌浓度范围的研究较少;对单一类型土壤矿物锌吸附的研究相对较多,而对不同类型矿物复合体或有机物质与土壤矿物复合体(这些复合体在土壤中是普遍存在的)锌吸附的研究相对较少。锌吸附量一般随土壤有机质含量的增加而增大,但外源有机质对土壤锌吸附过程和机理的影响较为复杂,其对锌吸附起促进作用还是抑制作用,主要取决于外源有机质的组成[19-20]。

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Advances in soil properties' effect on zinc absorption

ZHANG Hui-min[1,2,3], LÜ Jia-long[1], XU Ming-gang[2], LIU Hong-xia[3]

(1 *College of Resource and Environment, Northwest A & F University, Yangling, Shaanxi* 712100, *China*;
2 *Institute of Agricultural Resources and Regional Planning, Chinese Academy of Agricultural Sciences, Beijing* 100081, *China*;
3 *College of Agronomy, Henan University of Science and Technology, Luoyang, He'nan* 471003, *China*)

Abstract: Effect of soil properties, which includes pH, organic matter, clay minerals, temperature, competitive cations and coexisting anions in soil solution, in the process of soil zinc absorption is reviewed. The mechanisms of the varying amount of soil zinc absorption with the pH value, the content of organic matter, clay mineral types, soil temperature and coexisting ion species in soil solution are also summarized. Besides, existing problems and further research are also discussed.

Key words: soil properties; zinc absorption; heavy metal pollution; pollution amelioration

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