合成有机物对厌氧消化抑制的可逆性机理分析*

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编要 总结出抑制性合成有机物从厌氧消化系统内清除的 4 种主要作用途径,即厌氧降解作用、厌氧污泥吸附作用、挥发作用和随出水流出作用。从厌氧消化中各大类微生物之间相互平衡、协同作用的关系出发,分析了合成有机物对厌氧消化抑制的可逆性机理图式。 对厌氧消化抑制的可逆性机理,并提出了抑制性合成有机物对厌氧消化抑制的可逆性机理图式。 关键调 厌氧消化,合成有机物,厌氧降解作用,厌氧污泥吸附作用,挥发作用。

众多的研究资料表明,合成有机物对厌氧消化的抑制具有可逆性,但对可逆性机理尚缺乏系统的分析。本文结合笔者近年来在该方面的研究和国内外有关资料,对作为厌氧抑制可逆性的先决条件——合成有机物由厌氧系统内清除的主要作用途径进行了总结;从厌氧消化中各大类微生物相互平衡、协同作用的关系出发,在理论上就合成有机物对厌氧消化抑制的可逆性机理进行了分析。

I 系统内合成有机物清除的主要途径

一般认为,随着系统内抑制性合成有机物通过各种途径逐渐被清除,其对厌氧消化的抑制可逐渐得以消除,即抑制具有可逆性。系统内合成有机物清除的主要途径可归纳为厌氧降解作用、厌氧污泥吸附作用、挥发作用及随出水流出作用等4种。

1.1 厌氧降解作用

一些可降解的合成有机物,在与厌氧消化系统接触初期表现出了抑制性,但随着该合成有机物的降解,其抑制可以得到消除。

图 1 是酚类物质厌氧间歇抑制性试验中得到的几种酚类物质影响下的平均相对活性逐日变化曲线。由图 1 可知;苯酚、间甲酚、邻甲酚等酚类物质,在与厌氧消化系统接触初期表现出了抑制性,但随着培养时间的延长,抑制被消除,且最终(45d)累积产气量高于对照。这表明,这些酚

类物质对厌氧消化产生抑制,但最终可以消除抑制并能被厌氧降解。

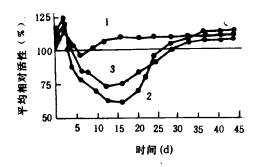


图 1 厌氧间歇抑制性试验结果^{1)**}
1. 苯酚(100mg/L) 2. 邻甲酚(100mg/L) 3. 对甲酚(100mg/L)

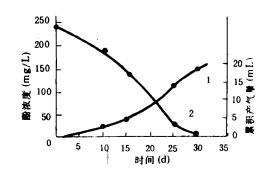


图 2 苯酚厌氧降解性试验结果 1. 产气量 2. 酚浓度

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图 2 为苯酚厌氧降解性能研究中得到的累积产气量和发酵液中残存苯酚浓度逐日变化曲线^[1],可以看出。酚作为基质与厌氧微生物接触初期表现出了抑制性,但随着酚的厌氧降解(残存苯酚浓度降低),其抑制逐渐被消除,最终完全被降解为 CH₄ 和 CO₂。

由于生理特性不同,产甲烷细菌对抑制性合成有机物较为敏感,而发酵性细菌则相对较能承受这种抑制。系统内的合成有机物可以通过发酵细菌的分解作用而被清除,使抑制被消除,同时其分解产物进入厌氧微生物的食物链,最终被分解为 CH₄ 和 CO₂。

以上分析表明,由于发酵性细菌的分解作用,可以从系统内清除抑制性合成有机物,消除抑制。因此,厌氧降解作用是抑制性合成有机物从系统内清除的主要途径之一。

1.2 厌氧污泥吸附作用

厌氧污泥对液根中的抑制性合成有机物具有吸附作用,使液相中合成有机物的浓度因此而降低,为抑制的消除创造了良好的环境条件。

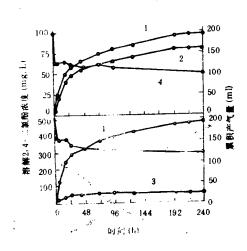


图 3 2.4-二氯酚厌氧间歇抑制性试验结果[2]
1. 对照累积产气量 2. 对照+100mg/L 2,4-二氯酚 累积产气量 3. 对照+500mg/L2,4-二氯酚聚积 产气量 4. 溶解态 2,4-二氯酚浓度

图 3 为 2,4-二氯酚厌氧间歇抑制性试验中所得的累积产气量及上清液中 2.4-二氯酚残留浓度的变化曲线^[2]。由图 3 可知:①2,4-二氯酚

对厌氧消化产生了抑制;②上清液中 2,4-二氯酚残留浓度除在初始阶段有一个显著的降低外,其后的 10d 内其含量基本不变。这表明:2,4-二氯酚难以生物降解,而初始阶段其浓度值的显著下降显然是因为厌氧污泥的吸附作用所致。

为证实厌氧污泥对抑制性合成有机物的吸附及其对消除抑制的作用,L. D. Johnson 等人将厌氧活性污泥浓缩、干燥后制成失去生物活性的钝化粉状固体,并将该粉体投入受合成有机物抑制的厌氧系统内,图 4 为试验结果。由图 4 可以看出,无论是六氯环戊二烯或是六氯乙烷对厌氧消化产生抑制时,投加钝化粉体的抑制消除速度都快于无粉体投加的对照,且投量越大,抑制消除速度越快。

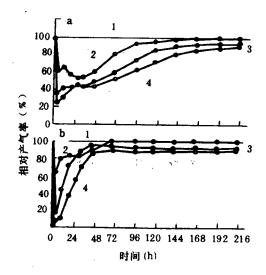


图 4 投加钝化固体的抑制性试验结果[2]

- a. 六氯环戊二烯(100mg/L) b 六氯乙烷(50mg/L)
 - 1. 对照
- 2. 未投纯化固体
- 3. 投 1g 钝化固体 4. 投 5g 钝化固体

以上对试验结果的分析表明: 厌氧污泥对系 统内的抑制性合成有机物具有吸附作用,而且这 种吸附作用有利于消除抑制。

如同合成有机物在水环境沉积物中的吸附^[3],厌氧污泥的吸附包括两种机制:一是厌氧污泥中的有机质((包括厌氧微生物及其代谢残小)对有机物的"溶解"作用,即分配作用;二是厌氧污泥中的无机矿物质对合成有机物的表面吸

附作用,即吸附作用。由于系统内厌氧污泥完全被水饱和,因此其对合成有机物的吸附作用机理主要是分配作用。而分配作用的大小取决于合成有机物的辛醇-水分配系数的大小用厌氧污泥中有机质含量的多少,即辛醇-水分配系数越大、厌氧污泥中有机质含量越多,吸附作用越强。

厌氧污泥对抑制性合成有机物的吸附,只是相间的转移,即液相浓度降低而固相浓度升高,其本质上并未转化或排出。但这种相间的转移对消除抑制具有积极意义,为未吸附抑制性合成有机物的厌氧微生物恢复代谢活性创造了良好的环境条件。正因为如此,从消除抑制角度考虑亦将其归纳为合成有机物清除的途径之一。

需要指出,吸附对消除抑制的积极作用还有 待于进一步的深入研究。

1.3 挥发作用

挥发作用是合成有机物由液相进入气相的 重要传质途径。同样,挥发作用也是抑制性合成 有机物由消化液中清除的主要途径。厌氧消化中 抑制性合成有机物的挥发,目前尚无试验研究资 料,在此仅从理论上作一简单分析。

在厌氧消化消化过程中抑制性合成有机物 的挥发具有以下几点特殊性:

- (1)厌氧消化中不断产生的沼气气泡增大了传质面积,强化了挥发。大量的气泡形成了一个个相互独立的挥发传质小单元,因此厌氧消化中挥发传质的气液两相接触面积远大于表层的气液两相界面面积。
- (2)系统内厌氧污泥对合成有机物的吸附作用,使液相中的真实浓度小于总浓度,因此,实际的传质推动力要小于表观上的传质推动力。
- (3)沼气气泡的不断逸出和排除,使气相不断得以更新,从而增大了挥发过程的气膜传质推动力。
- (4)沼气的不断产生和排除,有利于减小气膜和液膜厚度,降低传质阻力。

由于厌氧消化中气液两相传质的上述特点, 使抑制性合成有机物在其中的挥发不同于一般 水环境中的挥发,上述特殊性所引起的综合效应 是增大抑制或减小其挥发速率,由合成有机物的 性质而定。

尽管厌氧消化中合成有机物的挥发具有上述特殊性,但也基本遵循合成有机物从水中挥发的一般规律。亨利定律常数 H 基本反映了合成有机物挥发的快慢及其速率控制过程[4]。

1.4 随出水流出作用:

在连续或半连续的厌氧消化系统内,抑制性 合成有机物可随出水排出系统,从而由系统内清 除掉。

图 5 为甲醛厌氧半连续抑制性试验的结果^[5]。可以看出;接触 m 甲醛而受到的抑制能很快得以消除,迅速恢复产气,而长期接触时在30d的试验期间内一直没有产气。这表明排去含抑制性合成有机物的发酵液,可以消除其对厌氧消化的抑制。

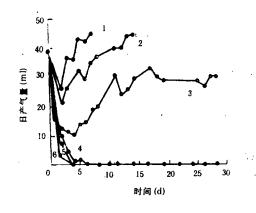


图 5 厌氧半连续抑制性试验结果

- 1. 接触 1h 甲醛(300mg/L) 2. 接触 1h 甲醛(600mg/L)
 - 3. 接触 in 甲醛(1800mg/L)

4、5、6. 长期接触甲醛(300、600、1800mg/L)

在连续的厌氧消化系统内,合成有机物随出水流出的速率主要取决于系统的水力停留时间 (HRT)的长短。因此,若抑制性合成有机物偶然进入连续的厌氧消化系统,即受到抑制冲击负荷时,可随出水流出使抑制性物质由系统内清除,且系统水力停留时间越短,抑制性物质随出水流出速率越快,系统内压氧微生物代谢活性恢复速率也越快。从这一意义上说,具有短水力停留时间的厌氧消化系统,有利于抑制性物质的清除,系统的稳定性较高。

综上所述,抑制性合成有机物从系统内清除的主要途径可归纳为厌氧降解作用、厌氧污泥吸附作用、挥发作用及随出水流出作用等 4 种。抑制性合成有机物性质不同,上述 4 种途径的作用大小不同,如可降解的抑制性合成有机物,厌氧降解作用可能是它的主要清除途径,而其它途径也将同时平行起作用。

2 含成有机物厌氧抑制的可逆性机理分析

2.1 几点假定

在分析合成有机物对厌氧消化抑制的可逆性机理时,先作如下几点合乎实际的假定:

- (1)假定抑制性合成有机物可通过前述的 4 种途径或其它存在的途径由系统内逐渐清除掉, 这是抑制可逆性的最基本前提。
- (2)假定抑制性合成有机物对非产甲烷菌无抑制而抑制了产甲烷菌的代谢活性。这是基于两大类菌群不同的生理特性而提出的一般假定,当然也有例外的情况,如邻位氯苯甲酸抑制了分解苯甲酸的产氢产乙酸细菌,而降解乙酸的产甲烷细菌则不受抑制[6]。
- (3)假定抑制程度不十分严重,即不至使细菌的活性完全丧失,难以恢复。当然这一假定是相对的,据笔者的试验观察,很多种合成有机物即便抑制相当严重,几十天停止产气,但最终仍可恢复产气。

2.2 抑制的可逆性机理分析

厌氧消化系统内存在着一个种群繁多、关系复杂的微生物区系,对基质的厌氧降解是区系中各种微生物相互平衡、协同作用的结果。这种相互平衡、协同作用的关系对抑制性合成有机物的厌氧抑制尤为重要,它可能使抑制放大,也可以消除抑制。有关因抑制性有机物诱发有机酸积累和氢分压升高引起的抑制放大,笔者已在另文中作过分析[7],在此着重讨论抑制的可逆性机理。

抑制性合成有机物通过各种途径逐渐由系统内清除出去,其对产甲烷细菌的抑制随之逐渐消除。就参与厌氧消化的整个微生物区系而言,除抑制性有机物引起的一次抑制之外,尚有因产甲烷菌受抑制而诱发的有机酸积累和氢分压升

高导致的二次抑制^[8]。对产甲烷细菌而言,有机 酸积累的抑制主要是由于 pH 值的降低,氢分压 升高的抑制主要是对氧化氢的乙酸积累营养型 产甲烷菌(OHA)的基质竞争抑制。如果有机酸未 超过一定的限度,pH 值下降不多,则随着合成有 机物对产甲烷细菌的抑制逐渐被解除,其代谢活 性逐渐恢复,乙酸和 H₂ 作为其基质逐渐被代谢, pH 值逐渐升高,pH₂ 逐渐降低,其代谢活性可以 得到进一步的恢复。

另一方面,乙酸逐渐被代谢,乙酸积累造成的对产氢产乙酸细菌的反馈抑制^[7]也逐渐解除。同时,pH₂ 的降低,也使产氢产乙酸细菌代谢有机酸(特别是丙酸)等中间产物的反应在热力学上有利。随着丙酸等较高级有机酸转化为乙酸、氢并为产甲烷菌所利用,使丙酸等较高级有机酸的积累逐渐消失,这样产甲烷菌受有机酸积累而被抑制的活性进一步得以恢复。

再者,随着乙酸、丙酸等相继被降解,积累的有机酸逐渐消失,发酵性细菌受到的反馈抑制也逐渐被解除。同时,由于 pH₂ 的降低,使发酵性细菌恢复正常的代谢途径,不再将电子沉积于中间产物上形成还原性中间产物,产甲烷细菌的代谢活性得到更彻底的恢复。

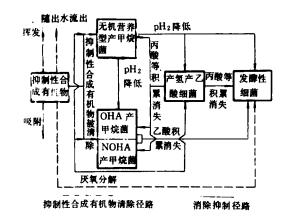


图 6 厌氧抑制可逆性机理图式

综上所述,合成有机物对厌氧消化抑制的可 逆性,关键在于产甲烷细菌代谢活性的恢复。随 着产甲烷细菌的代谢活性因抑制(下转第84页)

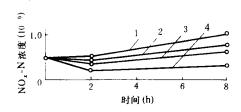


图 4 乙酸盐初始浓度与 NOx-N 之间 的变化关系(MLSS=4.60g/L)

1. $\hat{Ac}_{,0} = 0$ 2. $\hat{Ac}_{,0} = 75 \times 10^{-6}$

3. $A\bar{c}_{,0} = 125 \times 10^{-6}$ 4. $A\bar{c}_{,0} = 175 \times 10^{-6}$

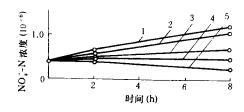


图 5 乙酸盐初始浓度与 NO_x-N 之间 的变化关系(MLSS=4.67g/L)

1. $A\bar{c}_{,0} = 0$ 2. $A\bar{c}_{,0} = 75 \times 10^{-6}$ 3. $A\bar{c}_{,0} = 125 \times 10^{-6}$ 4. $A\bar{c}_{,0} = 175 \times 10^{-6}$ 5. $A\bar{c}_{,0} = 210 \times 10^{-6}$

响较大。并且与乙酸盐对除磷效果影响相似,随 着乙酸盐(钠)投加量的增加,NOx-N的去除效

(上接第 64 页)性物质通过各种途径被清除而得以部分恢复,借助于厌氧消化中各大类微生物之间偶联的生化反应,从而彻底消除抑制。

图 6 为笔者归纳以上分析提出的厌氧抑制可逆性机理图式。

3 结语

- (1)抑制性合成有机物由系统内清除的主要途径可归纳为厌氧降解作用、厌氧污泥吸附作用、挥发作用及随出水流出作用4种,抑制性物质性质不同,清除的主要途径不同,而其它途径将平行起作用。
- (2)随着抑制性有机物由系统内被清除,借助于厌氧消化中各大类微生物之间的相互平衡、

率不断提高。因为生物脱氮除磷工艺的活性污泥微生物菌群体系中,存在具有反硝化作用的除磷菌^[8],而反硝化过程需要有机物参加。因此,乙酸盐(钠)的投加对 NOx⁻-N 去除效果的影响较NH⁺-N的大。

3 结论

- (1)废水中乙酸盐(钠)的含量对 PO-P 和 NO-N 去除效果的影响较 NH↓-N 的明显。
- (2)随着乙酸盐(钠)初始浓度的增加,循序间歇式生物脱氮除磷工艺的 PO¾-P、NOŢ-N 的去除率相应提高。其中,乙酸盐(钠)的最低起始浓度为 125×10-6,但超过 215×10-6后,便发生污泥膨胀现象。

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协同作用的关系,使诱发的有机酸积累抑制和氢分压升高的抑制逐渐被消除,最终使厌氧消化转入正常,其抑制的可逆性机理可归纳为图 6 所示的图式。

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Abstracts

Chinese Journal of Environmental Science

chem., Qingdao Univ., Qingdao 266071); Chin. J. Environ. Sci., 15(1), 1994, pp. 42—45

The adsorptions of cationic, disperse, reducible, neutral, active and direct dyes on bentonite are studied respectively and the decolorization effects of treating dye- containing aqueous solution by using bentonite adsorption-flocculation method and only flocculation method are compared. The decolorization rate of the former will be $40\,\%-200\,\%$ higher than that of the latter. Using 0.01% of bentonite with 0.005% of PAC can decolorize the dye-containing wastewater by $94\,\%-100\,\%$, where in the dye consists mainly of cationic dye.

Key words: bentonite, adsorption, flocculation, treatment of wastewater, organic dye.

Treatment of Effluent Containing Cu Ions by Means of a Packed Bed Electrochemical Reactor. Xu Wenlin, Wang Yaqiong (Taiyuan University of Technology, Taiyuan 030024): Chin. J. Environ. Sci., 15(1), 1994, pp. 46—49

A treatment process for effluent containing Cu ions is studied by means of a packed bed electrochemical reactor which is designed using one dimensional reactor model. Experimental results show that such a process particularly suitable for the treatment of the diluent effluent and the treated water can meet the requirement of the outlet concentration $< 1 \times 10^{-6}$; the factors affecting the effluent treament process, such as Cu ions input concentration, operation temperature, operation voltage, solution flow rate, effluent conductivity and the kind of the packed materal, are also discussed. This process is economically viable and provides an effective way of removing trace metal based on the assessment of the experimental process.

Key words: effluent containing Cu ions, packed bed electrode, electrochemical reactor, wastewater treatment.

Studies on the Treatment of Pharmaceutical Wastewater with Upflow Anaerobic sludge Blanket. Cheng Yu et al. (The Research Institute of Environmental Protection for Pharmaceutical Industry of Shenyang 110026); Chin. J. Environ. Sci., 15(1), 1994, pp. 50—52

In this paper, described were some research results about the treatment of wastewater from Vitamin-C, SD and glucose prodution processes at a normal temperature with upflow anaerobic sludge blanket. The reactor has a volume of 100 litres, at a fermentation temperature of $17-24^{\circ}\text{C}$ and the influent COD_{cr} of 3000-5000 mg/L. The organic load was 3-6kg COD/(m³ · d), the hydraulic retention time (HRT) was 18-24h and the rate of gas generation reached to $0.3\text{m}^3/\text{kg}$ COD with 70%

mechane in the gas. The COD_{cr} removal was up to 90%. All the experimental results were satisfactory. This process is found appropriate for treating the lower concentration pharmaceutical wastewater under the anaerobic condition.

Key words: upflow anaerobic sludge, blanket granular sludge, methanosarina, total volatile acid.

Survey on Municipal Domestic wastes Composting Technology in Mainland China. Chen Shihe (School of Environmental Engineering, Tongji University, / Shanghai 200092); Chin. J. Environ. Sci., 15 (1), 1994, pp. 53—56

This article deals with a general survey on the composting technology for municipal domestic wastes in mainland China, including: (1) the history of composting technology for municipal domestic wastes: initial stage, development and research stage, and application stage; (2) studies on composting technology: microorganism characteristic in composting process, oxygen delivery mechanism, composting process, factors affecting composting process, specialpurpose machinery, engineering of composting technology, and existing problem; (3) the trend of composting technology for municipal domestic wastes in mainland China. This article gives a detailed and complete description on the evolution, current status and prospects of composting technology for municipal domestic wastes in mainland China.

Key words: municipal domestic wastes, composting technology.

Monitoring Methods for Genetically Engineered Microorganisms in the Environment. Tong Yongyi (Institute of Microbiology and Epidemiology, Academy of Military Medical Sciences, Beijing 100071); Chin. J. Environ. Sci., 15(1), 1994, pp. 57—60

This paper deals with the monitoring principle and methods for genetically engineered microorganisms (GEM) in the environment, including the requirements of marker system on GEM for monitoring purpose, some recently developed marker systems and the monitoring methods for environmental GEM culture method, immunological method, genetic method, bioluminescent method and application of flow cytometry.

Key words: genetically engineered microorganism (GEM), environment, monitor.

Analysis of the Reversible Mechanism of Inhibition by Synthetic Organics in Anaerobic Digestion. Bian Rulin (Department of Environmental Engineering, Xi' an Institute of Metallurgy and Construction Engineering, Xi' an 710055): Chin. J. Environ.

Abstracts

Chinese Journal of Environmental Science

Sci. 15(1),1994,pp. 61-64

Four ways for removing inhibitive synthetic organics from an anaerobic system, including anaerobic degradation, sorption onto sludges, volatilation and washout are reviewed in this paper. Based on the relationship of interaction equilibrium between micro-organism communities in the anaerobic system, a reversible mechanism of the anaerobic inhibition by synthetic organics is analysed, and the diagram types of the reversible mechanism of inhibition are also proposed.

Key words: anaerobic digestion, synthetic organics, reversible mechanism of inhibition.

Relationship between Fusarium Toxins and Some Diseases. Zhang Hong, Li Jilun (College of Biological Sciences, Beijing Agricultural University, Beijing 100094); Chin. J. Environ. Sci., 15(1), 1994, pp. 65—68

In this article reviewed were the acute, subacute and chronic poisonings of some Fusarum Toxins to animal and human beings. Acute Fusarum toxins poisoning can cause Leukoencephalomalacia (LEM), Alimentary Toxic Aleukia (ATA), Fusariotoxicosis, etc; subacute poisoning causes Kashin-Beck's disease and Keshan disease; and chronic poisoning may cause cancers. It is emphasized that Fusarum Toxins in natrue are very dangerous to the health of both animal and human beings.

Key words: Leukoencephalomalacia (LEM), Kashin-Beck's disease, Keshan disease.

Progress and Reseath Needs in Flocculation Science. Chang Qing (Department of Environmental Engineering, Lanzhou Railway College, Lanzhou 730070); Chin. J. Environ. Sci. 15(1), 1994, pp. 69—72

In this article reviewed are some important progresses in floculation area, including those in design and operation diagram, physical model for rapid mixing, determination of optimum coagulant dosages, inorganic polymeric coagulants, selection of optimum treatment configuration. Some reseach needs were presented, including model reseach, descriptive work, optimal process design, and development of new coagulants.

Key words: coagulation, flocculation.

Analysis of The Combined Effects of Exposure to Multiple Pesticides on Fetal Development. Pan Xiaoqin (Dept. of Environmental Health, Tongji Medical University, Wuhan 430030); Chin. J. Environ. Sci., 15(1), 1994, pp. 73—74

In this paper analysed are the data from a prospective epidemiological investigation on women

whose pregnancy outcomes occurred during the period 1988 - 1989 in a defined rural population (about 120000 in total) in Yingchen county. There were 5674 women studied. According to the numbers of the pesticides which had ever been used by their families during their gestation period, the subjects were classified into eight cohorts and the occurring various adverse relative risks for pregnancy outcomes of each cohort were calculated. The results showed that the more the numbers of pesticides exposed, the more the risk for occurring spontaneous abortion and birth defect. There might be existed dose-response relationship between the numbers of pesticide categories and the adverse effects on fetal development. It is concluded that multiple pesticides used simultaneousely could have interacted with each other. Such combined effects were more significant during the earlier stage of pregnancy.

Key words: pesticide, pregnancy outcome, interaction, combined effect.

Investigation into the Effects of Environmental Noise on the Health of Population Living Around Coal Mines. Fu Changying, Wu Zhengyi (Shanxi Provincial Institute for Labor Health and Occupational Disease, Taiyuan 030012); Chim. J. Environ. Sci. .15(1).1994.pp. 75—78

To refer to PRC's standard for environmental noise, two groups of population which exposed to the noise above 50 dB(A) and below 50 dB(A) were selected from Guandi coal mine in western mountain region, Taiyuan, and 256 men above 16 years old were taken as the investigative subjects in this study. The results of measurement were that the greatest values of environmental noise measured outdoor and indoor were 75 dB(A) and 63 dB(A), respectively. All of these values have exceeded the PRC's standard for environmental Therefore, the results shown that living, working and studing under this condition have injuried effects on population's nerve system and hearing to a certain extent and the injury extent was associated closely with living- years. The positive rate of neurasthenia in population living for above 10 years and exposed to above 50 dB(A) was 34. 28%, while that exposed to below 50 dB(A) was 13. 35%, the hearing injury of voice frequency in population living for above 10 years and exposed to 50 dB(A) was 34.7% while that living for below 10 years was 29. 59% and there were statistically significant differences between both above at P < 0. 05.

Key words: population, noise intensity, environmental noise in coal mine, health damage.