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UV Photolysis Coupled with H₂O₂ Oxidation for Accelerated Sulfamethoxazole (SMX) Degradation and Mineralization

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ABSTRACT

Antibiotics are widely used to treat human infections and in livestock and poultry breeding, and they often are detected in surface water. Sulfamethoxazole (SMX) is one widely used antibiotic due to its broad-spectrum application, stability, and low cost. This work investigated advanced oxidation techniques used for SMX degradation and mineralization. The approaches were UV photolysis alone (UV), H₂O₂ oxidation alone (H₂O₂), and UV photolysis coupled with H₂O₂ oxidation (UV/H₂O₂). Experimental results indicated that coupling UV photolysis with H₂O₂ oxidation significantly accelerated the SMX removal rate and also increased the degree of SMX mineralization. The SMX removal rates by UV/H₂O₂ were 31% to 73% greater than that with UV alone for the range of initial SMX concentrations tested (20 to 80 mg/L). For UV photolysis coupled with H₂O₂ oxidation, H₂O₂ was decomposed into hydroxyl radicals, which attacked chemical bonds of SMX intermediates to bring about TOC removal and release of NO₃⁻, NH₄⁺, and SO₄²⁻.

Keywords: Sulfamethoxazole, UV photolysis, peroxide

oxidation (H₂O₂), degradation, mineralization

INTRODUCTION

It is common that residual pharmaceuticals are discharged into natural environments, resulting in environmental contamination, because the pharmaceuticals, especially for antibiotics, are widely used for the treatment of patients and for livestock breeding throughout the world.^[1-2] It is usually impossible for human or animal bodies to absorb them completely. Therefore, the residual drugs are directly discharged into natural environment with wastewaters from hospitals, livestock and poultry farms, and dwellings. The residual drugs form usually permanent contamination, if the wastewater could not be treated by advanced technologies. More pharmaceutical active compounds (PhACs) have been detected recently in urban wastewater treatment plants, surface water, even waterworks.^[3] Antibiotics have certain toxicity and inhibition to micro-organisms and algae even in the microgram or milligram levels.^[4-5] Different organisms (bacteria, algae, rotifers, crustaceans and fish) have been respectively tested with sulfamethoxazole, erythromycin, oxytetracyclin, ofloxacin, lincomycin, and clarithromycin to show that acute toxicity level is in the level of mg/L, while the chronic toxicity appears at concentrations in the level of µg/L, mainly to algae.^[6] Even worse is that coexistence of a variety of antibiotics in the aqueous environments will lead to multi-drug resistant micro-organisms.^[7] The qualitative risk assessment ranking relative to probability and potential severity on human and environmental health effects is: antibiotics > sex hormones > cardiovascular > antineoplastics.^[8] So how to degrade and mineralize these pharmaceutical components has been given increasing attention.^[9-10]

Sulfamethoxazole (SMX), with a molecular formula of C₁₀H₁₁N₃O₃S, molecular weight of 253.27, is one of sulfonamides (SAs) widely used for curing and cultivation due to its broad-spectrum antibiotic action, curative effect, stable nature, and low cost. It was reported that China had become a main country producing and exporting sulfonamides, and the export trade in the international market accounted for around 70%.^[11] SAs are hardly biodegraded due to its antibiotic nature and chemical stability.^[12-14] An indisputable fact is that emissions of pharmaceutical wastewater are proportional to the output of pharmaceutical products. Unfortunately, normal biological methods are usually powerless for the antibiotics' degradation, although they are effective for biodegradation of recalcitrant compounds in many cases. Hence, these pharmaceuticals, together with other pollutants like insecticides and environmental hormones should be considered to be treated with advanced oxidation processes (AOPs), including UV/H₂O₂, UV/O₃, UV/TiO₂ and Fe²⁺/H₂O₂, which is usually thought as one of effective treatment methods for degradation of recalcitrant organic compounds.^[15-16]

Compared with these methods, ultra violet irradiation is one of more effective methods for pharmaceuticals degradation. SMX is easier to be degraded under UV

irradiation as it is light sensitive to UV photolysis by absorbing UV light with wavelength less than 310 nm, but the pharmaceuticals are only transferred into the intermediates, which give lower mineralization,^[17] or lower TOC (or COD) removal percentage, even with TiO₂ powder as the photocatalyst. It is obvious that these intermediates are still harmful to natural environment and human health; therefore, to enhance mineralization extent will be an important issue for treatment of wastewater containing residual pharmaceuticals.

AOPs are effective methods for treatment of pharmaceuticals and are accepted by people for degradation of antibiotics containing SMX, but their degradation or mineralization extent is affected by many factors, like initial pharmaceuticals concentration, oxidant species and its dosage etc.^[18-19]

Among AOPs, combination of hydrogen peroxide and UV (UV/H₂O₂) is valuable to be employed for treatment of pharmaceuticals as its practicability,^[20-21] although hydrogen peroxide and UV irradiation can be used alone to facilitate the degradation of certain contaminants. Hydrogen peroxide is a very strong oxidizing agent that is capable of destroying some halogenated compounds and most nonhalogenated compounds in aqueous media.^[22-23] UV light itself is also very capable of degradation by initiating bond cleavage. However, the range of contaminants UV can degrade by itself is limited. The degradation kinetics can also be very slow. The combination of the two treatments - hydrogen peroxide and UV - can create a very fast and efficient process for degradation of SMX.

In this work, a photolytic circulating bed reactor (PCBR) was used for degradation and mineralization of SMX with three protocols: UV photolysis alone (UV), peroxide (H₂O₂) oxidation alone, and UV photolysis coupled with H₂O₂ oxidation (UV/H₂O₂). The extent of mineralization of SMX was the primary focus.

MATERIALS AND METHODS

Reactor System

The PCBR was adopted in this work, as it allows the solution containing SMX to be illuminated fully by UV light, and H₂O₂ added can be mixed with the solution quickly in the reactor. The reactor was made of quartz glass with 230 ml of working volume and was similar to photolytic circulating bed biofilm reactor (PCBBR),^[24] but with no biofilm present. The solution was driven by air aeration provided from the bottom of the reactor to circulate in the reactor during the operation. The main wavelength of ultra violet (UV) was 254 nm and light intensity was 0.46 mW/cm², and the distance between the light and reactor was 10 cm.

Chemicals

SMX (99.9%) was obtained from Aldrich Chemical Company. Acetonitrile of HPLC-grade was purchased from TEDIA (OH, USA) and used for analysis of SMX concentration. Peroxide (H₂O₂, 30% in H₂O) and other reagents were of analytical grade and obtained from

Shanghai Chemical Reagent Company.

Experimental Methods

Preparation of SMX solution

SMX was dissolved with de-ionized water obtained from a Millipore Milli-Q system, and the pH was adjusted to 7 with NaOH of 0.1M to obtain an original solution with 500 mg/L of SMX as the stock solution, which was stored in the refrigerator with 4°C. SMX solutions with different concentrations were prepared by dilution before every experiment. The pH values were adjusted by using 0.1 M HCl or NaOH to give a pH of 3 or 10 according to the experimental demand.

Degradation of SMX by three protocols at different pH values

The stock SMX solution was diluted to a concentration of 60 mg/L and was treated with H₂O₂ oxidation alone (H₂O₂), UV photolysis alone (UV), and coupled H₂O₂ oxidation alone with UV photolysis (UV/H₂O₂) at different pH values to investigate the effect of pH on SMX removal rate. Before treatment, the pH of SMX solution was adjusted to pH of 3, 7, and 10. The solution was stirred with air in the PCBR and was irradiated with UV light, and the samples were taken in a certain interval to analyze SMX concentrations.

Decomposition of H₂O₂ under UV irradiation

H₂O₂ was illuminated with UV light or ambient light to investigate its decomposition. The experiments were carried out for 90 min, and samples were taken at every 30 min to measure H₂O₂ concentrations in order to measure hydroxyl radical concentrations, as H₂O₂ can be decomposed into hydroxyl radicals under UV irradiation.

UV compared with UV/H₂O₂ for SMX removal rates

The solutions were diluted to 20, 40, 60, or 80 mg/L for parallel degradation experiments in which the solutions were adjusted to pH 3 before each experiment was carried out. For UV experiment, the solution containing SMX was only irradiated by UV light without H₂O₂ added, and for UV/H₂O₂ experiment, 10-mM H₂O₂ was added to the PCBR and mixed well with the solution by aeration under UV irradiation. During the experiments, the samples were also taken in a certain interval time to analyze SMX concentration. Based on the experiments, experimental data were regressed to get SMX removal kinetics, which would be compared to evaluate the protocols.

Mineralization of SMX

For the experiment of SMX mineralization, the stock solution was also diluted into 60 mg/L, and pH was respectively adjusted to 3 before the experiment. The solutions were respectively treated for 18 h by UV and UV/H₂O₂ to investigate TOC reduction. For the UV/H₂O₂ process, 10 mM H₂O₂ was added into the reactor before treatment. Similarly, samples were taken at intervals to measure TOC concentration.

Analytical Methods

The SMX concentration was measured by a high performance liquid chromatograph (HPLC, model: Agilent 1100, USA) equipped with a DAD detector with wavelength of 250 nm and ZORBAX SB-C18 column (5 μ m, 4.6 \times 250 mm). The mobile phase was a mixture of acetonitrile water solution (30:70, v/v) and the flow rate was 1 ml/min.

KMnO₄ method was used to measure residual H₂O₂, based on the reaction of $2\text{MnO}_4^- + 16\text{H}^+ + 5\text{C}_2\text{O}_4^{2-} = 2\text{Mn}^{2+} + 10\text{CO}_2\uparrow + 8\text{H}_2\text{O}$, which can be then used to determine $\cdot\text{OH}$ generation during UV/H₂O₂ process.^[25]

Total Organic Carbon (TOC) was measured by a TOC automatic detector (model: Elementar LiquiTOC, Germany), pH was measured with a pH meter (model: pHs-25c, China), and UV light intensity was measured with a light meter (model: BG-2254, China).

Cations and anions were measured by ion chromatography with DIONEX (USA) model ICS-5000. For the ammonium cation, the separation column was IonPac CG12A (50 \times 4mm, S/N 022328), and the mobile phase (eluent) was 20 mM (methanesulfonic acid) MSA at a flow rate of 1.0 mL/min. For the sulfate, nitrate, and nitrite anions, the separation column was IonPac AG18 (50 \times 4mm), and the eluent was mixed solution of Na₂CO₃ (4.5mM) and NaHCO₃ (0.8mM) at a flow rate of 1.0 mL/min.

RESULTS AND DISCUSSIONS

Effect of Initial pH on SMX Removal using the three protocols

Figure 1 gives the SMX removals at different pHs and for the different protocols. It is obvious that the SMX removal rates were faster by UV/H₂O₂ than by UV alone or H₂O₂ alone at all pH values. For the same protocol, lower pH was superior to higher pH for SMX removal. For all pH conditions, H₂O₂ alone was powerless to degrade SMX. CO₂ was also brought into the reactor because of air aeration, and CO₂ turned into HCO₃⁻ and CO₃²⁻ under higher pH conditions. HCO₃⁻ and CO₃²⁻ are very efficient $\cdot\text{OH}$ radical scavengers, based on $\text{CO}_3^{2-} + \cdot\text{OH} \rightarrow \text{CO}_3^{\cdot-} + \text{OH}^-$ and $\text{HCO}_3^- + \cdot\text{OH} \rightarrow \text{CO}_3^{\cdot-} + \text{H}_2\text{O}$, and carbonate species (CO₃²⁻ and HCO₃⁻) competed with organic contaminants for hydroxyl radicals. In this study, the HCO₃⁻ can be ignored at pH = 10; so CO₃²⁻ was the main $\cdot\text{OH}$ radical scavengers.^[26,27]

Due to greater radical scavenging at high pH, SMX removals were faster at pH 3 than at pH 7 and 10 (Fig. 1). Hence, the follow up experiments for UV photolysis alone (UV) and coupled UV photolysis with H₂O₂ oxidation (UV/H₂O₂) were only carried out at pH 3.

Based on the experimental results from Fig. 1, the hydroxyl radicals, formed from H₂O₂ under UV irradiation,^[28] played the important role in degradation of SMX, and this is consistent with the oxidation potential of hydroxyl radicals (2.80eV) being higher than that of the H₂O₂ (1.77eV).^[29,30] Furthermore, UV alone was superior to H₂O₂ alone for SMX degradation because SMX is photosensitive to UV. In following experiments, therefore, the H₂O₂ oxidation alone was no longer considered.

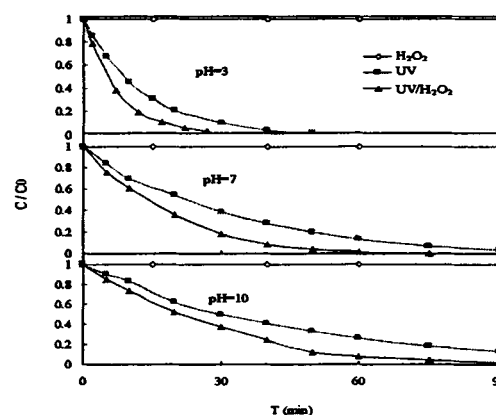


Fig. 1. Effect of pH and protocol on the kinetics of SMX degradation (C₀ = 60 mg/L).

Effect of UV on H₂O₂ Decomposition

To investigate H₂O₂ decomposition with and without UV irradiation, H₂O₂ was successively added into 230 mL of pure water in PCBR, and both solutions contained H₂O₂ at 5.3 mM. The experiments were carried out for 90 min, and samples were taken at every 30 min to measure H₂O₂ concentration. Figure 2, which gives the H₂O₂ concentrations, demonstrates that H₂O₂ was little decomposed without UV irradiation, but was decomposed gradually with UV irradiation. The experimental results suggest that hydroxyl radicals ($\cdot\text{OH}$) were generated from H₂O₂ under UV irradiation based on $\text{H}_2\text{O}_2 + h\nu \rightarrow 2\cdot\text{OH}$ during the process of UV/H₂O₂.^[31] Comparing SMX removal by the three protocols in Figure 1 supports that SMX removal rate was accelerated due to more hydroxyl radicals in the protocol of UV/H₂O₂. SMX was degraded under UV irradiation alone as it is photoactive substance,^[19] but its removal rate was slower than that under UV/H₂O₂.

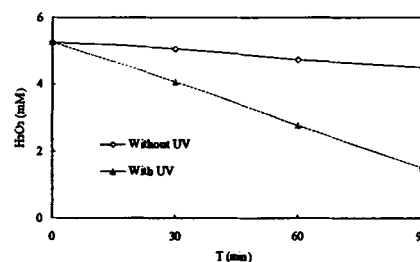


Fig. 2. H₂O₂ change with and without UV irradiation

Comparison with SMX Removal Rates Under UV and UV/H₂O₂

Protocols UV alone and UV/H₂O₂ were performed with initial SMX concentration of 20, 40, 60, or 80 mg/L, and the results are shown in Figure 3. The most important finding is that SMX removal rates by UV/H₂O₂ were substantially faster than that by UV alone.

The results in Figure 3 suggest that SMX removal fits one-order kinetics, and corresponding kinetics data and correlation coefficients (R^2) are shown in Table 1. For all initial SMX concentrations, the first-order loss coefficient k was larger by UV/H₂O₂ than by UV alone. Table 1 shows that k value was always higher with the

protocol of UV/H₂O₂ than that with UV alone, as hydroxyl radicals have higher oxidation potential. According to the data of Table 1, for the same protocol, the k value increased with decreasing initial SMX concentration, which suggests that the production of hydroxyl radicals was rate limiting.

Comparing the bottom panel of Figure 3 with Figure 2 indicates that the rate of SMX decrease was obviously higher than with H₂O₂ alone, which further supports that faster SMX removal was the result of reaction by the hydroxyl radical.

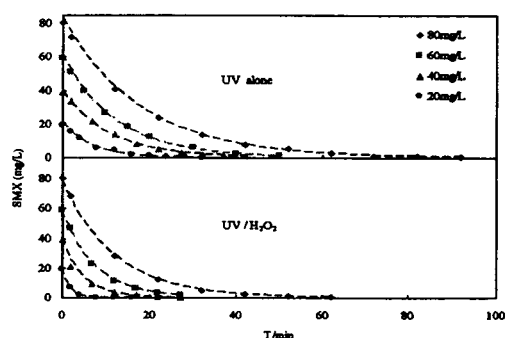


Fig. 3. Effect of initial SMX concentration of UV and UV/H₂O₂ degradation. Table 1 gives the first-order loss coefficient corresponding to the curves.

Table 1. The first-order loss rate coefficient for SMX degradation experiments

Protocol	Initial SMX concentration (mg/L)	k (1/min)	R^2
UV alone	80	0.057	0.997
	60	0.082	0.998
	40	0.093	0.997
	20	0.154	0.988
UV/H ₂ O ₂	80	0.083	0.999
	60	0.130	0.999
	40	0.203	0.985
	20	0.559	0.999

Mineralization of SMX

SMX intermediates could be harmful, although SMX was degraded completely within 2 h in this study. So, full mineralization is usually the main goal of the treatment of wastewater containing SMX. The TOC removal is an important index to measure the SMX mineralization extent in the experiments.

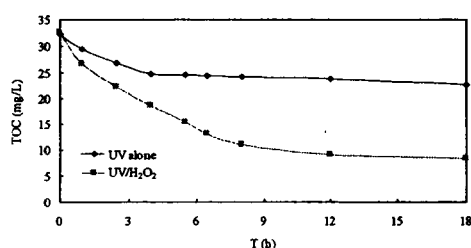


Figure 4. TOC removal for the two protocols

Fig. 4 gives the TOC removals for 18 hours by two protocols. TOC continually declined over 4 to 8 hours, and UV/H₂O₂ gave considerably greater removal than UV alone: 75 %

versus 30 %. These experimental results imply that hydroxyl radicals played also an important role in mineralization of SMX.

Ions released from SMX structure

SMX molecular structure contains benzene sulfonyl amino, aromatic primary amino, isoxazole ring and benzene ring, in which isoxazole ring and benzene ring are connected by benzene sulfonyl amino and aromatic primary amino. In this study, SMX solution of 0.24 mM (60 mg/L) was treated with 10 mM H₂O₂ added and without H₂O₂ added under the same UV irradiation for 8 h to investigate N and S elements released from the SMX structure. Figure 5 shows the increase in NH₄⁺, NO₃⁻, and SO₄²⁻ during the treatments; N was released mostly in NH₄⁺ and NO₃⁻ forms, NO₂⁻ appeared in a trace level (data are not shown in Figure 5), and S was SO₄²⁻. For 10 mM H₂O₂ added together with UV irradiation, NH₄⁺ concentrations increased to about 0.24 mM between 2 to 3 hours, and the SO₄²⁻ concentration also increased to about 0.24 mM at the same time, while NO₃⁻ concentration did not appear until 0.5 hour and increased to 0.06 mM gradually then. All of this means that one third N was released as NH₄⁺ and all S element was released as SO₄²⁻ from SMX structure during UV/H₂O₂ process. SO₄²⁻ was generated from benzene sulfonyl amino during the process according to the SMX structure. Shu et al.^[21] proposed that SMX is first decomposed into isoxazole and benzene rings, which are further decomposed due to being attacked by hydroxyl radicals. The results in Figure 5 are consistent with this pathway.

NH₄⁺ and SO₄²⁻ concentrations did not increased from hour 2 to hour 8 (Figure 5), but the NO₃⁻ concentration did not appear until 0.5 hour. Daneshvar et al. proposed^[22] that NO₃⁻ ion was released from isoxazole ring, in which =N= was broken to release NO₂⁻ at first, and then transferred into NO₃⁻ immediately, together with isoxazole ring broken. The experimental result suggests that SMX was decomposed into isoxazole ring and benzene ring sooner rather than the rings opened.

For no H₂O₂ addition protocol, NH₄⁺ and SO₄²⁻ concentration increased gradually and total releasing amounts for 8 h were respectively only 48% and 33% of the UV/H₂O₂ protocol. Figure 5 shows that no NO₃⁻ ion was released during the UV alone process, which suggests that it was difficult for UV alone to open isoxazole ring or benzene ring, because of absence of hydroxyl radical. In another word, isoxazole ring did not release NO₃⁻ unless it was attacked by the hydroxyl radical, e.g. NO₃⁻ was the ring opened products of isoxazole. The experimental results also explained the difference between protocols UV alone and UV/H₂O₂ for SMX degradation.

Comparing Figure 3 to Figure 5 shows that, while it took less than two hours to remove SMX to zero, NH₄⁺ and SO₄²⁻ ions were released only after more than 2 hours. Thus, these ions were released gradually from SMX intermediates, instead of from SMX structure directly.

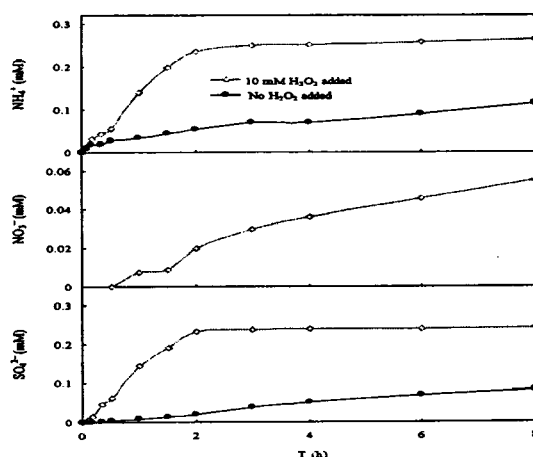


Fig. 5. Effect of H_2O_2 addition on NH_4^+ , NO_3^- and SO_4^{2-} ions release under UV irradiation

CONCLUSIONS

SMX was degraded by three protocols: H_2O_2 oxidation alone, UV photolysis alone, and UV photolysis coupled with H_2O_2 oxidation. The experimental results indicate that H_2O_2 alone was not able to degrade SMX, while SMX was degraded by UV photolysis alone, but the SMX removal rate was accelerated by coupling UV photolysis with H_2O_2 oxidation. Depending on the initial SMX concentration, the removal rate was enhanced by 30% to 73% by coupling UV with H_2O_2 , and SMX mineralization also increased. SMX removal and mineralization were accelerated due to more hydroxyl radicals generated from H_2O_2 under UV irradiation. For UV photolysis coupled with H_2O_2 oxidation, H_2O_2 was decomposed into hydroxyl radicals under UV irradiation, which attacked SMX intermediates. Leading to TOC removal percentages and release of inorganic ions.

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Efficient ammonia removal from swine manure using anammox granular process

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EXTENDED ABSTRACT

With rising environmental concerns on potable watersafety and eutrophication, increased media attention and tighter environmental regulations, managing animal wastes in an environmentally responsible and economically feasible way can be a challenge. Nitrogen removal has become a major focus in swine manure treatment since nitrogen is the nutrient concerning the application amount of the manure produced in accordance with an increasing number of governmental regulations. The objective of this study was to develop a potential swine manure treatment process that can achieve high nitrogen standards at reduced costs. As a novel, autotrophic and cost-effective alternative to the traditional biological nitrification/denitrification removal process, anammox process was proved to be effective for swine manure nitrogen removal. A rapid decrease of NO₂⁻ and NH₄⁺ was observed during incubation with wastewater from activated sludge deodorization reactor and its corresponding control artificial wastewaters. The presence of organic carbon had limited effect on the performance of anammox granular sludge, highly dependent on COD to N ratios.

These results demonstrated that anammox system substantially organic carbon benefited livestock productivity.

Key words: anammox; granular sludge; nitrogen; organic carbon; swine manure;

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The Regional Breeding Structure Affect for Soil Phosphorus Balance of Farmland System ——A Case of Xiangtan County

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ABSTRACT

For exploring the regional planting and breeding structure's influence on soil phosphorus balance of farmland system, this paper analysed the breeding structure of Xiangtan County regional farmland system based on the statistical data of Hunan province. The result shows that soil phosphorus balance of Xiangtan County regional farmland system mainly depends on phosphorus inputting of fertilizers and manure as well as the phosphorus output caused by production of farm crops. The average of soil phosphorus surplus about arable and cultivated area presented a more clear upward trend. And counting from 2000 to 2011, it were 25.59 kgP · hm⁻² and 13.49 kgP · hm⁻². The reason can be attributed to a large number of input of fertilizer containing phosphorus within regional farmland system.

Keywords: Regional breeding structure; Farmland system; Soil phosphorus balance; Xiangtan County

Phosphorus is one of the most important nutrient-limiting factors in agricultural production, and also is the major limiting factor of aquatic eutrophication^[1-2]. In crop production, most soils can produce satisfying output by replenishing nitrogen and phosphorus with mineral fertilizer and (or) excrements of livestock. However, the nitrate pollution to surface and underground water^[3] and phosphorus load from agricultural production are main factors causing eutrophication of lake, river and sea water^[4-5]. Thus, many economically advanced countries have regarded soil phosphorus surplus causing by the balanceless management of nutrients as an important environment problem rather than agronomical one^[6].The