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Nitrogen Degradation Kinetic Analysis in Different Subsurface Constructed Wetlands

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ABSTRACT

In this study, the kinetic models of pollutant degradation in different wetlands were studied. The kinetic equations were deduced and the kinetic simulation of the main pollutants such as NH_3-N and TN was completed by the experimental data, and the dynamics of the pollutant degradation simulation model were applied to simulate the effect of the reaction kinetics model on the removal of contaminants in horizontal steel slag subsurface wetland (HSSSW) and horizontal volcanic subsurface wetland (HVSW). The results showed that the first order reaction kinetics model could obviously simulate the effect of main pollutants such as NH_3-N and TN in two kinds of subsurface wetlands. The correlation coefficient R^2 of the dynamic linear model was 0.9640 and 0.9600 in HSSSW, respectively, and the correlation coefficient R^2 of the HVSW was 0.9365 and 0.9709, respectively. The degree of fitting and correlation was very good. Besides, the simulation results showed that the degradation of the main pollutant was of great reference value for the design and operation of the practical subsurface wetland.

INTRODUCTION

Degradation of pollutants in subsurface wetlands was a complex process, and physical, chemical, biological and other reactions were involved in the systems (Sudarsan et al. 2015, Bulent et al. 2006, Chang et al. 2004, Tanner et al. 2007, Tao et al. 2006, Lin et al. 2002). The dynamic processes occurring in the system were the main factors that determined the degradation effect of pollutants (Chang et al. 2007). The research of sewage treatment technology of subsurface constructed wetland had attracted more and more attention because of its good effect on nitrogen and phosphorus treatment and ecological value (Mays et al. 2001, Yue et al. 2008). More and more scholars had begun to study the degradation of pollutant in subsurface wetland more deeply (Zhang et al. 2008, Zhang et al. 2007, Fisher et al. 2001). Moreover, in the process of pollutant degradation, the design and operation provided better data and theoretical basis.

At present, the mathematical models widely used to simulate the removal of contaminants in subsurface wetlands were the first order reaction model, the Monod model, the ecological dynamics model, etc. (Richardson et al. 1999, Reddy et al. 1998, Zht et al. 1997). Among them, the first-order reaction kinetics model was the most suitable mathematical model for simulating the removal of contaminants in subsurface wetlands because of its convenience and accuracy (Wang et al. 2013, Tanner et al. 1997). Many scholars extensively applied the basic equations of the first-order reaction kinetics to the design of subsurface wetlands and to predict the removal efficiency of pollutants from sewage, such as organic matter, nitrogen and phosphorus, in the subsurface flow wetland system. This study mainly analyses the effect of simulating subsurface flow wetland on the degradation of pollutants based on reaction kinetic equation.

MATERIALS AND METHODS

Subsurface wetland systems: The experiment was carried out in a laboratory with a controlled environment in Tangshan of P.R. China. The horizontal subsurface wetland systems consisted of two $1m^2$ wetland mesocosms (1.6m long × 0.6m broad × 0.6m deep). Gravel, with a particle diameter of 15-25mm, was laid at the bottom of the two systems, and the depth was 0.10m. Steel slag and volcanic ash were laid respectively in the middle layers of the two wetlands, both with particle diameters of 6-10mm and depth of 0.40m. The sieving soils were laid in the uppermost layers, the depth of which was 0.05m. *Phragmites* and reed mace were planted in the soils with the interplanting ratio

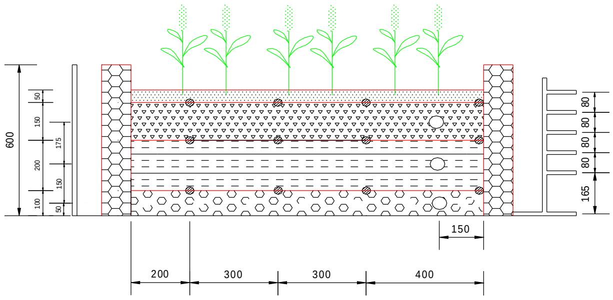


Fig. 1: Schematic diagram of horizontal subsurface wetland.

of 1:1. The horizontal steel slag subsurface wetland would be represented by HSSSW and horizontal volcanic subsurface wetland by HVSW in the following parts of this paper. The schematic diagram of the main apparatus is shown in Fig. 1.

Simulation methods: In the process of subsurface flow, the water flow and wetland dissolved oxygen were very vulnerable to the external environment. The first order kinetic model derived the subsurface flow as a steady state system, and it was considered that the ideal pollutant degradation in the subsurface wetland was mainly related to the time and the distance of the sewage, and in the whole process, the oxygen capacity of the wetland was enough to meet the metabolic activity of aerobic microorganisms.

On the basis of the above assumptions, the first-order kinetics of the pollutant in subsurface flow with time is usually as follows:

$$\frac{dC}{dt} = -k_T C \quad ...(1)$$

In above equation:

dC/dt - Removal rate of pollutants ($mgL^{-1}d^{-1}$)

k_T - The volume rate constant at temperature T

C - Concentrations of Pollutants in Submerged (mg/L)

When the reaction is a second order kinetic reaction, the equation is as follows:

$$\frac{1}{C_{out}} = \frac{1}{C_{in}} + k_T t \quad ...(2)$$

In above equation:

C_{out} - Concentration of effluent pollutants (mg/L)

C_{in} - Concentration of influent pollutants (mg/L)

t - Hydraulic retention time of the system (d)

As is shown in the above equation, the half-life of the second-order kinetic reaction is inversely proportional to the influent contaminant concentration. In the case of known influent pollutant concentrations in subsurface wetlands, the volumetric rate constant k_T could be determined by plotting the $(1/C_{out}-1/C_{in})$ ~ t relationship, where the slope of the curve is k_T. From the above results, it was concluded that the degradation of the main pollutants in the sewage could be simulated by the first order and second order kinetic equations. It was clear from the formula that if the degradation reaction of the pollutants was in accordance with the first order kinetic reaction, the curve of ln (C_{out}/C_{in})~t was a straight line and $(1/C_{out}-1/C_{in})$~t if the degradation of the pollutants was in accordance with the second order kinetic reaction, the ln(Cout/Cin)~t curve was a straight line and the $(1/C_{out}-1/C_{in})$~t curve was also a straight line.

Table 1: Quality of raw water.

Parameter	Unit	Concentration
pH	-	6.5~8.0
Chemical oxygen demand (COD)	mgL^{-1}	53.2~85.7
Ammonia nitrogen (NH_3-N)	mgL^{-1}	9.5~12.6
Total nitrogen (TN)	mgL^{-1}	15.5~21.7
Total phosphorus (TP)	mgL^{-1}	0.74 ~2.35

Influent quality: The raw wastewater was collected from river water of Douhein Tangshan. The composition of the influent used in all the experiments is shown in Table 1.

Experiment methods: The removal rates of NH_3-N and TN in subsurface flow wetland system were calculated and analysed by Origin 8.0 software. The dynamic equation of $\ln(C_{out}/C_{in})$ and $1/C_{out}-1/C_{in}$ kinetic equation and the linear correlation were analysed.

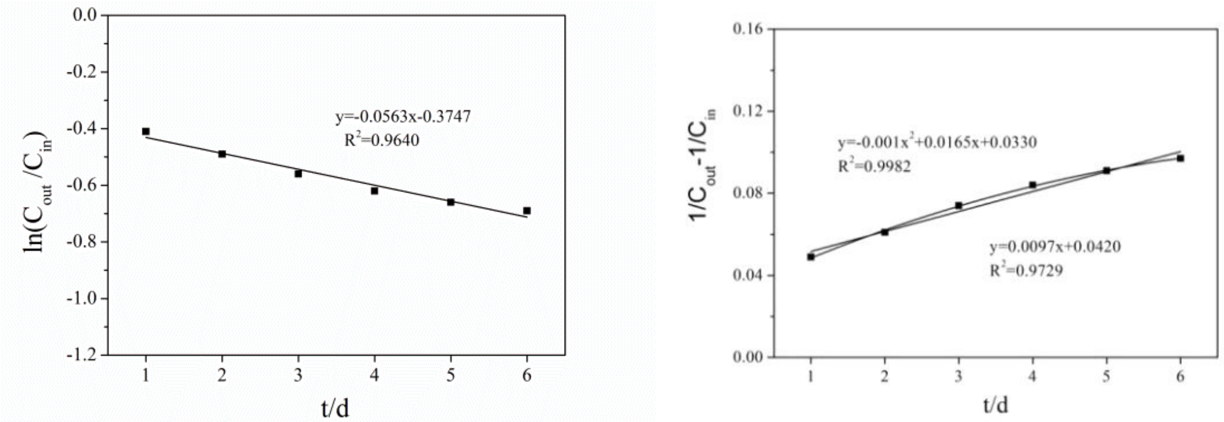
RESULTS AND DISCUSSION

The simulation of ammonia nitrogen removal: In order to study the kinetic model of NH_3-N degradation in submerged wetland, the NH_3-N concentration was 10.2mg/L, and the data were processed according to the NH_3-N value of the effluent from the subsurface wetland. The degradation time of NH_3-N in the subsurface wetlands was 6 d, the degradation effect of NH_3-N in each subsurface wetland is shown in Table 2.

The $\ln(C_{out}/C_{in})$~t and $(1/C_{out}-1/C_{in})$~t were plotted on the basis of the relationship between C_{out} with NH_3-N effluent concentration and hydraulic retention time in horizontal slug subsurface wetlands and HVSW. And the reaction kinetics equation of NH_3-N degradation in subsurface flow wetland was established.

According to the fitting curve, the kinetic simulations of removing NH_3-N from HSSSW and HVSW were as follows:

1. As is shown in Fig. 2(a), in the first-order reaction kinetics curve of NH_3-N degradation in horizontal-slug subsurface wetland system, $\ln(C_{out}/C_{in})$ was a straight line about t, that is, the first order reaction kinetic equation



(a) (b)

Fig. 2: Fitting curve of reaction kinetic NH_3-N degradation for HSSSW.

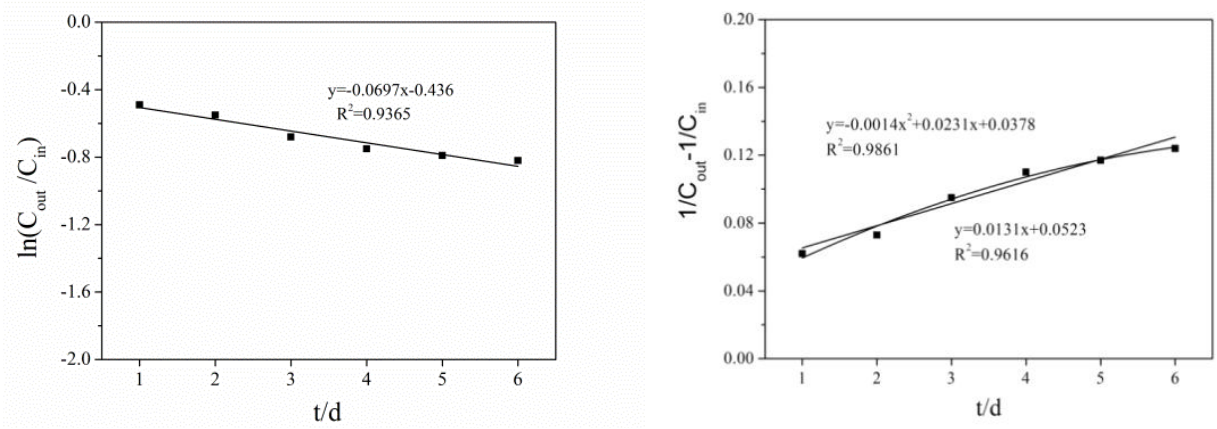
Table 2: Relevant parameter of NH_3-N degradation effect for each wetland at various HRT.

HRT/d	HSSSW				HVSW			
	C_{out}	$\ln(C_{out}/C_{in})$	$1/C_{out}-1/C_{in}$	Removal rates(%)	C_{out}	$\ln(C_{out}/C_{in})$	$1/C_{out}-1/C_{in}$	Removal rates(%)
1	6.80	-0.41	0.049	33.3	6.23	-0.49	0.062	38.9
2	6.28	-0.49	0.061	38.4	5.86	-0.55	0.073	42.5
3	5.81	-0.56	0.074	43.0	5.17	-0.68	0.095	49.3
4	5.48	-0.62	0.084	46.3	4.81	-0.75	0.110	52.8
5	5.29	-0.66	0.091	48.1	4.65	-0.79	0.117	54.4
6	5.13	-0.69	0.097	49.7	4.51	-0.82	0.124	55.8

was $\ln(C_{out}/C_{in})=-0.0563x-0.3747$, and the correlation coefficient $R^2=0.9640$. The first-order kinetics equation was the rate constant $k_T=0.0563$ for the degradation of NH_3-N in the subsurface wetland. As is shown in Fig. 2(b), we know that the binomial equation of the second order reaction kinetics of NH_3-N degradation was $1/C_{out}-1/C_{in}= -0.001x^2+ 0.0165x + 0.0330$, and the correlation coefficient R^2 was 0.9982. The linear equation was $1/C_{out}-1/C_{in}=0.0097x+0.0420$, and the correlation coefficient $R^2=0.9729$. The second order kinetic equation could be used to decompose the NH_3-N volume rate constant $k'_T=0.0097$.

2. As is shown in Fig. 3(a), in the first-order reaction kinetics curve of NH_3-N degradation in horizontal-volcanic subsurface flow wetland system, $\ln(C_{out}/C_{in})$ was also a straight line about t, that is, the first-order reaction kinetics equation of the equation was $\ln(C_{out}/C_{in})= -0.0697x-0.436$ and the correlation coefficient $R^2=0.9365$ of the simulated equation. The first-order kinetic equation showed that the volume rate constant $k_T=0.0697$ for NH_3-N degradation in subsurface wetland. From Fig.3(b), the binomial reaction equation of the second-order reaction kinetics of NH_3-N degradation was $1/C_{out}-1/C_{in}=-0.0014x^2+0.0231x+0.0378$, and the correlation coefficient $R^2=0.9861$, the linear equation was $1/C_{out}-1/C_{in}=0.0131x+0.0523$, the correlation coefficient $R^2=0.9616$, and the second-order kinetic equation for wetting degradation rate of NH_3-N, and the $k'_T = 0.0131$.

To sum up, the correlation coefficient of the first order reaction kinetics equation is 0.93, which indicated that the first-order reaction kinetics model could simulate the subsurface flow wetland NH_3-N, the removal rate of NH_3-N in different subsurface wetlands gradually increased with the hydraulic retention time, and the removal of NH_3-N in the two subsurface wetlands was accordant with the increase of the residence time rate, and which was also increasing the law. In the second order reaction kinetics model, the correlation coefficient of the binomial equation in the two stage reaction was slightly larger than that of the linear model, which indicated that the correlation coefficient of $(1/C_{out}-1/C_{in})$~t was closer to the curve, namely, the first order kinetics equation was better than the second order kinetics equation for the removal of NH_3-N from the subsurface wetland. The kinetic simulations of removal with NH_3-N by subsurface wetlands were in accordance with the first-order reac-



(a) (b)

Fig. 3: Fitting curve of reaction kinetic NH_3-N degradation for HVSW.

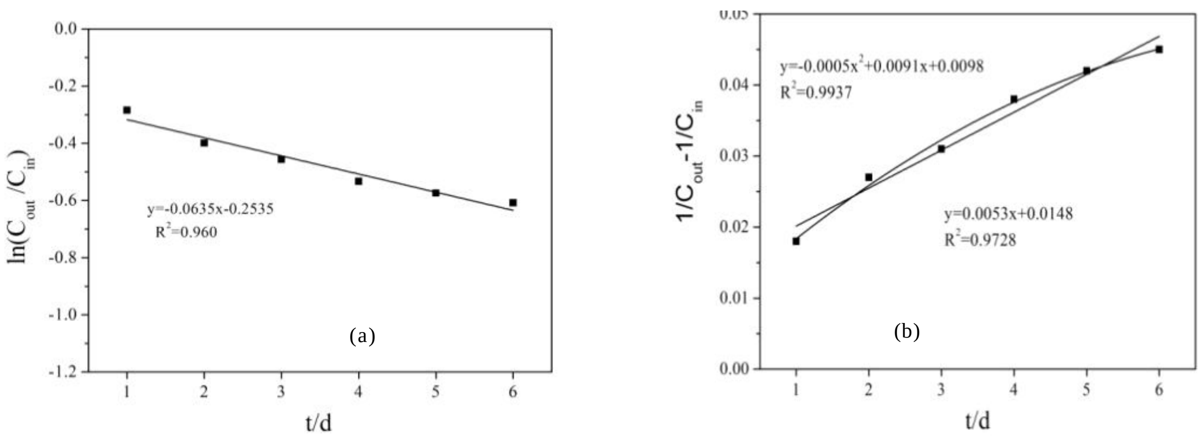
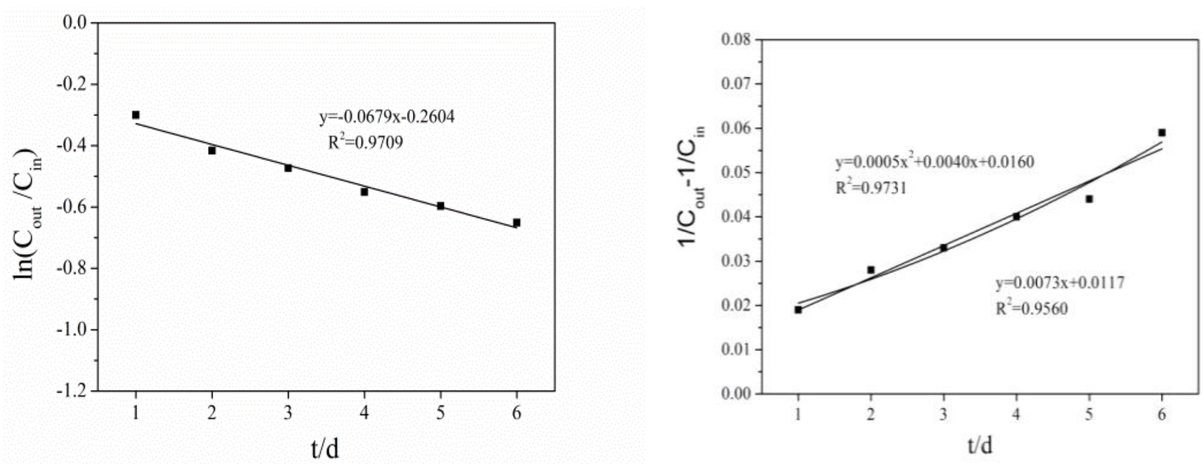


Fig.4: Fitting curve of reaction kinetic TN degradation for HSSSW.



(a) (b)

Fig.5: Fitting curve of reaction kinetic TN degradation for HVSW.

Table 3: Relevant parameter of TN degradation effect for each wetland at various HRT.

HRT/d	HSSSW				HVSW			
	C_{out}	$ln(C_{out}/C_{in})$	$1/C_{out}-1/C_{in}$	Removal rates(%)	C_{out}	$ln(C_{out}/C_{in})$	$1/C_{out}-1/C_{in}$	Removal rates(%)
1	13.92	-0.284	0.018	24.8	13.73	-0.300	0.019	25.9
2	12.41	-0.399	0.027	32.9	12.21	-0.416	0.028	34.0
3	11.73	-0.345	0.031	36.6	11.53	-0.473	0.033	37.7
4	10.86	-0.533	0.038	41.3	10.66	-0.551	0.040	42.4
5	10.42	-0.574	0.042	43.7	10.18	-0.597	0.044	45.0
6	10.07	-0.608	0.045	45.6	9.65	-0.651	0.059	47.8

tion kinetics equation.

In addition, in the first order reaction, the correlation coefficient of the horizontal slug subsurface flow wetland system linear regression equation was larger than that of the horizontal volcanic subsurface flow wetland system. This showed that the first order reaction dynamics model was effective to the HSSSW degradation NH_3-N and better than that of HVSW, but the horizontal volcanic wetland was smaller than that of HSSSW, which indicated that the removal efficiency of NH_3-N was lower than that of HVSW. The highest removal rate of HSSSW was 49.7%, and the highest removal rate of horizontal volcanic subsurface flow wetland system was 55.8%, and the average removal rate was better than that of HSSSW system. The first order kinetics model was a good mathematical model for simulating the degradation of NH_3-N in subsurface wetlands. The results showed that the degradation of NH_3-N in subsurface flow was consistent with the first order kinetics.

The simulation of total nitrogen removal: In order to study the dynamic model of TN degradation in subsurface wetland, TN was simulated with influent concentration of 18.5mg/L. According to the TN value of effluent from the subsurface flow, the data were processed for the effluent. The hydraulic retention time was 6d, The degradation effect of TN in the subsurface wetland is shown in Table 3.

According to the relationship between the C_{out} and the hydraulic retention time t, the relationship between $ln(C_{out}/C_{in})$~t and $(1/C_{out}-1/C_{in})$~t was drawn from the relationship between the HSSSW and horizontal volcanic subsurface flow wetland. And the reaction kinetics equation of TN degradation in subsurface flow wetlands was determined.

According to the fitting curve, the kinetic simulation of removing TN from horizontal steel slug subsurface flow wetland and horizontal volcanic subsurface flow wetland is as follows:

1. As is shown in Fig. 4(a), in the first order reaction kinetics curve of the HSSSW system, TN was a straight line about t, that is, the first order reaction kinetics equation $ln(C_{out}/C_{in}) = -0.0635x-0.2535$, the correlation coefficient $R^2=0.960$, and the first order kinetic equation for the degradation rate of TN in subsurface wetlands was $k_T=0.0635$. From Fig. 4(b), the binomial reaction equation of the second order reaction kinetics of TN degradation was $1/C_{out}-1/C_{in}=-0.0005x^2+0.0091x+0.0098$, and the correlation coefficient $R^2=0.9937$, and the linear equation is $1/C_{out}-1/C_{in}=0.0053x+0.0148$. The correlation coefficient $R^2=0.9728$, and the second order kinetic equation showed that the volume rate constant $k'_T=0.0053$.
2. As is shown in Fig. 5(a), in the first order reaction kinetics curve of TN degradation of horizontal volcanic subsurface flow wetland system, $ln(C_{out}/C_{in})$ was also a straight line about t, that is, the first order reaction kinetic equation was for the $ln(C_{out}/C_{in}) = -0.0679x-0.2604$, the correlation coefficient $R^2=0.9709$ of the simulated equation, the first order kinetic equation for the degradation rate of TN in subsurface wetland was $k_T=0.0697$. From Fig. 5(b), the binomial reaction equation of the second order reaction kinetics of TN degradation was $1/C_{out}-1/C_{in}=0.0005x^2+0.0040x+0.0160$, and the correlation coefficient $R^2=0.9731$. And the linear equation was $1/C_{out}-1/C_{in}=0.0073x+0.0117$. The correlation coefficient $R^2=0.9560$, and the second order kinetic equation was used to describe the rate constants $k'_T=0.0073$.

In conclusion, the correlation coefficient of the first order reaction kinetics equation was above 0.95, which indicated that the first order reaction kinetics model could well simulate the subsurface flow wetland, which was the HSSSW or horizontal volcanic subsurface flow wetland, the TN removal rate increased with the increase of hydraulic retention time, and the removal rate of TN in the two subsurface flow wetlands was increased with the increase of the residence time of the law. In the second order reaction kinetics model, the correlation coefficient of the binomial equation of the two-stage reaction was slightly larger than that of the linear simulation equation. It was shown that $(1/C_{out}-1/C_{in})$~t was closer to the curve, that is, the first order kinetics equation was better than the second order kinetics equation to simulate the dynamics of TN degradation in subsurface wetland. Therefore, the kinetic simulation of degradation of TN was in accordance with the first order reaction kinetics equation.

In addition, the correlation coefficient of the horizontal steel slag subsurface flow wetland system in the first order reaction was lower than that of the horizontal volcanic subsurface flow wetland system, which indicated that the first-order reaction kinetics model had a significant correlation with the HSSSW degradation TN, better than that of HVSW, and the horizontal velocity of volcanic subsurface flow wetland was lower than that of horizontal volcanic subsurface flow wetland, which indicated that the removal efficiency of TN to horizontal volcanic subsurface flow wetland was lower. In the data, the highest removal rate of horizontal steel slag subsurface flow wetland system was 45.6%, the highest removal rate of horizontal volcanic subsurface flow wetland system was 47.8%, and the average removal rate was better than that of HSSSW system. The first order kinetics model was a mathematical model which could simulate the degradation effect of TN on subsurface wetland.

CONCLUSION

In this research, the kinetic models of degradation of pollutants in the subsurface wetlands were proposed, the kinetic equation was deduced and the kinetic simulation of the main pollutants such as NH_3-N and TN was carried out by the experimental data, and the dynamics of the pollutants degradation simulation model was applied to simulate the effect of the reaction kinetics model on the removal of contaminants in the horizontal steel slag and HVSWs. The results showed that the first order reaction kinetics model could simulate the effect of main pollutants such as NH_3-N and TN in two kinds of subsurface wetlands. The HSSSW of correlation coefficient R^2 of the dynamic linear model was 0.9640 and 0.9600, respectively, and the correlation coefficient R^2 of the horizontal volcanic subsurface flow wetland was 0.9365 and 0.9709, respectively. The degree of fitting and correlation were very good. The simulation results showed that the degradation of the main pollutants in the subsurface wetland was of great reference value for the design and operation of the subsurface wetland.

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