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Vegetated Steel Slag Substrate Constructed Wetlands can Achieve High Efficiency Simultaneous Nitrogen and Phosphorus Removal

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Steel slag substrate constructed wetlands (SSCWs) can effectively remove phosphorus (P) from sewage through Ca-P precipitation and adsorption. Nonetheless, the disadvantages of a high pH value of the effluent and low nitrogen (N) removal efficiency limit the practical application of SSCWs. To improve these shortcomings, plant cultivation and combining steel slag with other substrate materials have been applied in SSCWs. However, related studies have not obtained a unanimous consensus elucidating such improvements. To accurately evaluate improvements, we statistically analyzed the experimental data reported in 27 related papers and found that combining steel slag with other substrate materials in SSCWs significantly increased the removal amount of total nitrogen (TN) (51.58 mg TN/L) and ammonium nitrogen (NH_4^+-N) (74.15 mg NH_4^+-N/L) but reduced the removal amount of total phosphorus (TP) (7.76 mg TP/L). In these combined substrate SSCWs, plant cultivation could compensate for the decline in TP removal amount and improve upon the simultaneous removal of N and P (6.02 mg TP/L, 62.18 mg TN/L, and 69.16 mg NH_4^+-N/L). Moreover, compared with vertical flow SSCWs, horizontal flow enables plant-cultivated and combined substrate SSCWs to achieve a higher TP removal capacity (6.38 mg TP/L). In addition, operational parameters, including temperature, hydraulic retention time (HRT), pH value, and influent concentration, significantly affected the N and P removal capacity of SSCWs. Our research results provide a theoretical reference for the design and operation of SSCWs for efficient N and P removal.

Keywords: steel slag, planting, constructed wetlands, nitrogen removal, phosphorus removal

INTRODUCTION

As early as the 1980s, research on the application of steel slag to remove phosphorus (P) began (Yamada et al., 1986). The use of steel slag, a by-product of the iron and steel industry, as a substrate in constructed wetlands (CWs) to treat nitrogen (N) and P in sewage (Park et al., 2016) provides broad prospects for the recycling of steel slag waste. Steel slag substrate CWs (SSCWs) remove pollutants through physical, chemical, and biological processes mediated by substrate, plants, and microorganisms. Among these components, the steel slag substrate plays a particularly prominent role in P removal, and the main mechanism is Ca-P precipitation and adsorption (Pratt et al., 2007). On the one hand, CaO in steel slag is hydrolyzed to form Ca-P precipitates with PO_4^{3-} in sewage (Baker et al., 1998; Kim et al., 2006). On the other hand, active sites such as metal oxide and hydroxyl oxide (Mo (OH)) sites adsorb P onto the surface of steel slag and gradually form hydroxyapatite (HAP) crystals (Drizo et al., 2006; Chazarenc et al., 2007). In column experiments of basic oxygen furnace steel slag, the PO_4^{3-} removal efficiency was higher than 99%, and the removal capacity reached 3.1 mg P/g (Blanco et al., 2016). The TP removal rate from urban sewage by vertical flow SSCWs can reach 76% (Ge et al., 2016). Vertical and horizontal flow SSCWs can be connected in series, and the total phosphorus (TP) removal rate from construction sewage can reach 62% (Barca et al., 2013).

However, the strong alkalinity of steel slag is not conducive to plant growth and microbial survival, and it leads to a high pH of the effluent, which is attributed to the low efficiency of N removal by plants and microbes. Although ion exchange adsorption between NH_4^+ and metal ions (such as Al^{3+}, Fe^{2+}, and Mn^{4+}) in steel slag can remove some ammonium nitrogen (NH_4^+-N) (Xu et al., 2019), when compared with microbial nitrogen removal, the nitrogen removed by adsorption is limited. This makes simultaneously removing N and P efficiently in SSCWs difficult. Combing steel slag with other materials, mixed or layered filling, might address these difficulties by relieving the strong alkalinity in SSCWs, whereas the reduced proportion of steel slag in the substrate could decrease P removal (Shen et al., 2020).

Due to the ability of plant roots to absorb N and P (Cui et al., 2015; Yun et al., 2015; Yuan et al., 2017; Saeed et al., 2020), as well as the active microbial metabolism of roots, plant cultivation in combined substrate SSCWs might be an effective way to compensate for the reduced P removal capacity of a combined substrate. The plants cultivated in these SSCWs are mainly common wetland plants, such as *Vetiveria zizanioides*, *Canna indica*, *Acorus calamus*, and *Phragmites australis*, which demonstrate high nutrient levels absorption rates and tolerance to saline and alkaline conditions. However, the role of plants in SSCWs has been controversial. Some studies showed that the death and decay of plants under excessively alkaline conditions can cause the release of P and reduce the removal amount of P (Lu et al., 2021; Zheng et al., 2021). In addition, the influence of operation parameters on the capacity of SSCWs to remove N and P also lacks a summative general mechanism. Based on these aspects, we systematically analyzed existing research results on SSCWs to clarify the following questions: 1) Can vegetated SSCWs improve the capacity to simultaneously remove N and P?, and 2) What is the general rule whereby operation parameters affect the capacity to remove N and P?

DATA COLLECTION AND STATISTICAL METHODS

Dataset Formation

In this study, a comprehensive literature search was conducted to collect research data on SSCWs. The databases considered mainly included the Web of Science, Scopus, and Springer Link. The main keywords used included CWs, steel slag, nitrogen removal and phosphorus removal. This search contained almost all studies on SSCWs. These studies are described in **Section 3**, and the results are summarized and discussed. Next, not all articles could be employed for further analysis because they were review articles, and certain articles did not contain data on N and P removal amounts. By reading the title, abstract, and text of the articles during screening, 27 articles (Huang and He, 2011; Wu et al., 2011; Xiong et al., 2011; Barca et al., 2013; Shilton et al., 2013; Barca et al., 2014; Ren et al., 2014; Shi et al., 2014; Cui et al., 2015; Ge et al., 2015; Hussain et al., 2015; Yun et al., 2015; Zhang et al., 2015; Blanco et al., 2016; Ge et al., 2016; Lu et al., 2016; Mohamed et al., 2016; Ahmad et al., 2017; Shi P. et al., 2017; Park et al., 2017; Yuan et al., 2017; Adera et al., 2018; Xu et al., 2019; Chen et al., 2020; Hamdan et al., 2020; Saeed et al., 2020; Wan et al., 2020) met our requirement and were finally selected for data analysis, which provided a highly uniform dataset and reliable results. Datasets of the substrate filling mode, plant cultivation, flow direction of CW, steel slag particle size (SSPS), temperature (T), hydraulic retention time (HRT), hydraulic loading rate (HLR), pH value (pH), influent concentration (C_{in}), total nitrogen (TN), NH_4^+-N, and TP removal amounts ($\Delta C = C_{in} - C_{out}$) were extracted from these articles, and some original data were modified.

Statistical Analysis

To reveal the influence of substrate filling mode, plant cultivation and flow direction on TP, TN, and NH_4^+-N removal, a single-factor analysis of variance was carried out of the TP, TN, and NH_4^+-N removal amounts achieved by CWs with steel slag substrate filling, layered steel slag and other substrate filling, mixed steel slag and other substrate filling, non-planted and planted CWs, and horizontal flow and vertical flow. Before analysis, the sample data must conform to a normal distribution, and the variance must be homogeneous. Otherwise, the data were converted until the above conditions were met, and variance analysis was subsequently performed. For the sample data that still did not meet the above conditions after conversion, a Kruskal–Wallis nonparametric analysis was performed. For example, during the grouping of the substrate filling modes, the NH_4^+-N removal data still did not conform to a normal distribution after conversion, so Kruskal–Wallis

TABLE 1 | Summary of steel slag substrate constructed wetlands studies carried out at different areas with various experiment scale treatment of scale, sewage type, plant, substrate, and removal rates.

Study	Scale	Sewage Type	Plant	Substrate	Removal rates (%)	Study Area
Baker et al. (1998)	Batch	Stock phosphate solution	No plants	50 wt% silica sand, 45 wt% limestone and 5 wt% BOF steel slag	PO_4^{3-}-P: 99	Canada
Drizo et al. (2006)	Batch	Stock phosphate solution	No plants	100 wt% EAF steel slag 79 wt% EAF steel slag and 21 wt % limestone	PO_4^{3-}-P: 100 PO_4^{3-}-P: 100	Canada
Kim et al. (2006)	Batch	Stock phosphate solution	No plants	Converter slag	PO_4^{3-}-P: 70–98	South Korea
Huang and He, (2011)	Laboratory	Septic tank sewage	*Canna indica* L	30 cm washed sand and soil mixture, 30 cm limestone and 10 cm steel slag from the top to the bottom	COD: 77 NH_4^+-N: 85 PO_4^{3-}-P: 96	China
Wu et al. (2011)	Laboratory	Low concentration domestic sewage	No plants	Steel slag 30 cm anthracite, 30 cm vermiculite and 30 cm steel slag from the top to the bottom	TP: 90.26 TP: 82.45	China
Xiong et al. (2011)	Integrated constructed treatment system	Secondary effluents	*Vetiver zizanioides* (L.) Nash	40 cm peat, 60 cm steel slag and 20 cm coarse sand from the top to the bottom	COD: 61.36 TP: 76.58 (removal rates for the vertical flow constructed wetland)	China
Barca et al. (2013)	Field experiments	Municipal wastewater	No plants	EAF steel slag BOF steel slag	TP: 44.71 TP: 58.82	France
Shilton et al. (2013)	Mesocosm	Real pond effluent	No plants	Steel slag	TP: 90	New Zealand
Barca et al. (2014)	Laboratory	Synthetic solution	No plants	EAF steel slag BOF steel slag	TP: 98 TP: 99	France
Shi et al. (2014)	Microcosm	Slightly polluted river water	No plants	1:2 mixture of zeolite and steel slag	COD: 57.55 NH_4^+-N: 62.77 NO_3^--N: 34.79 TP: 96.31	China
Yun et al. (2015)	Pilot	Domestic wastewater with a low phosphorus concentration	*Phragmites australis*	50 cm steel slag and 20 cm coarse gravel from the top to the bottom 50 cm modified steel slag and 20 cm coarse gravel from the top to the bottom	TP: 84 TP: 88	China
Ge et al. (2015)	Large scale demonstration	Polluted river water	*Phragmites australis*	Steel slag and gravel	COD: 73.5 TN: 23.2 TP: 53.5	China
Hussain et al. (2015)	Pilot	Septic tank sewage	No plants	10 cm washed limestone gravel, 57 cm BOF steel slag and gravel mixture and 10 cm basal sand from the top to the bottom	PO_4^{3-}-P: 98.6–99.8	Canada
Ren et al. (2014)	Laboratory	Synthetic wastewater	No plants	2.5 cm zeolite, 2.5 cm steel slag and 2.5 cm gravel from the top to the bottom	COD: 75.90 NH_4^+-N: 68.39 TN: 45.16 TP: 74.55	China
Zhang et al. (2015)	Laboratory	Secondary effluent from a municipal sewage treatment plant	*Phragmites australis*	10 cm cobble and rice husk, 25 cm steel slag and 20 cm limestone from the top to the bottom	COD: 66–83 NH_4^+-N: 100 TN: 100; TP: 81–90 (removal rates for the two-stage vertical flow constructed wetland)	China
Blanco et al. (2016)	Batch	Stock phosphate solution	No plants	BOF steel slag	PO_4^{3-}-P: 84–99	Spain
Lu et al. (2016)	Mesocosm	Rural household sewage	Aquatic plants	Soil, steel slag, gravel stone from the top to the bottom	COD: 79.7 NH_4^+-N: 80.0 TN: 74.4 TP: 83.5	China
Mohamed et al. (2016)	Pilot	Household graywater	No plants	12.7 cm clamshells, 12.7 cm steel slag and limestone mixture and	COD: 74	Malaysia

(Continued on following page)

TABLE 1 | (*Continued*) Summary of steel slag substrate constructed wetlands studies carried out at different areas with various experiment scale treatment of scale, sewage type, plant, substrate, and removal rates.

Study	Scale	Sewage Type	Plant	Substrate	Removal rates (%)	Study Area
				12.7 cm sand from the top to the bottom		
Ge et al. (2016)	Laboratory	Polluted urban river water	*Phragmites australis*	BOF steel slag	TP: 76	China
Park et al. (2017)	Microcosm	Hydroponic wastewater	*Iris pseudoacorus*	Rapid cooled BOF steel slag (RC-BOFS)	PO_4^{3-}-P: 94.2	South Korea
				75% coarse sand and 25% RC-BOFS	PO_4^{3-}-P: 89.3	
Shi et al. (2017a)	Microcosm	Synthetic wastewater	No plants	20 cm zeolites and 10 cm steel slag from the top to the bottom	TP: 80–90	China
Yuan et al. (2017)	Pilot	Domestic and agricultural wastewaters	No plants	50 wt% coarse sand, 30 wt% pebble aggregate, 10 wt% TiO_2 processing residue, 4 wt% wood chip, 3 wt% blast furnace slag, 3 wt% blast furnace slag	TN: 55 TP: 81	China
Ahmad et al. (2017)	Laboratory	Synthetic wastewater	No plants	High calcium EAF steel slag	PO_4^{3-}-P: 76–98	Malaysia
Adera et al. (2018)	Mesocosm	Dairy farm wastewater	No plants	EAF steel slag	DRP: 99	United States of America
Chen et al. (2020)	Pilot	Wastewater treatment plant secondary effluent	No plants	Ceramsite and steel slag	COD: 81.3 TN: 31.3 TP: 85.0	China
Xu et al. (2019)	Mesocosm	Simulated wastewater	*Acorus calamus*	10 cm sand and 30 cm Ti-bearing blast furnace slag from the top to the bottom	NH_4^+-N: 77.54 TN: 71.07 TP: 98.00	China
				10 cm sand and 30 cm converter steelmaking slag from the top to the bottom	NH_4^+-N: 59.23 TN: 53.02 TP: 96.00	
Hamdan et al. (2020)	Pilot	Domestic wastewater	No plants	Steel slag	NH_4^+-N: 91	Malaysia
Saeed et al. (2020)	Mesocosm	Leachate	*Vetiver*	5 cm stone,1 m steel slag, 1 m concrete block and 5 cm stone from the top to the bottom	COD: 40.4 NH_4^+-N: 91.3 TN: 30.3 TP: 91.6	Bangladesh

nonparametric analysis was performed. Then, samples with insufficient data were finally removed.

Next, the Pearson correlation coefficient is widely adopted to measure the degree of correlation between two variables. This value varies between −1 and 1. A negative value suggests a negative correlation, and a positive value indicates a positive correlation. To quantify the relationship between the TP, TN, and NH_4^+-N removal amounts and SSPS, T, HRT, HLR, pH, and C_{in}, a Pearson correlation coefficient matrix was established. In addition, to describe the interaction between the TP, TN, and NH_4^+-N removal amounts and the abovementioned operation parameters, redundancy analysis (RDA) was conducted.

To quantitatively describe the relationship between the TP, TN, and NH_4^+-N removal amounts and the operation parameters, a regression analysis method was applied. In a multiple linear regression model, the dependent variable is a linear function of the independent variables X_i, as follows:

$$Y = a + b_1X_1 + b_2X_2 + ... + b_nX_n \tag{1}$$

where Y is the predicted value of the dependent variable, and X_1, X_2, ... X_n are the independent variables. The dependent variables included the TP, TN, and NH_4^+-N removal amounts $\Delta C = C_{in} - C_{out}$ (mg/L), and the independent variables were the SSPS (mm), T (°C), HRT (d), HLR (m/d), pH, and C_{in} (mg/L). All variables inserted in the model were considered significant at $p < 0.05$.

We employed SPSS 26 software (IBM, United States) for variance analysis, the Kruskal–Wallis test for nonparametric analysis, and set the condition for statistical significance at $p < 0.05$. An RDA was conducted by Canoco 5. Also, R 4.0.3 was used for illustrations.

EVALUATION OF STEEL SLAG SUBSTRATE CONSTRUCTED WETLANDS

Applications of Steel Slag Substrate Constructed Wetlands

In the initial application stage, SSCWs stuffed with single steel slag as substrate were used to remove P from sewage with different P concentrations. Following that, SSCWs with a combined and modified substrate were used to comprehensively improve the quality of septic tank sewage (Huang and He, 2011; Hussain et al., 2015), domestic sewage (Wu et al., 2011; Yun et al., 2015; Mohamed et al., 2016; Hamdan et al., 2020), urban sewage (Barca et al., 2013), pond sewage

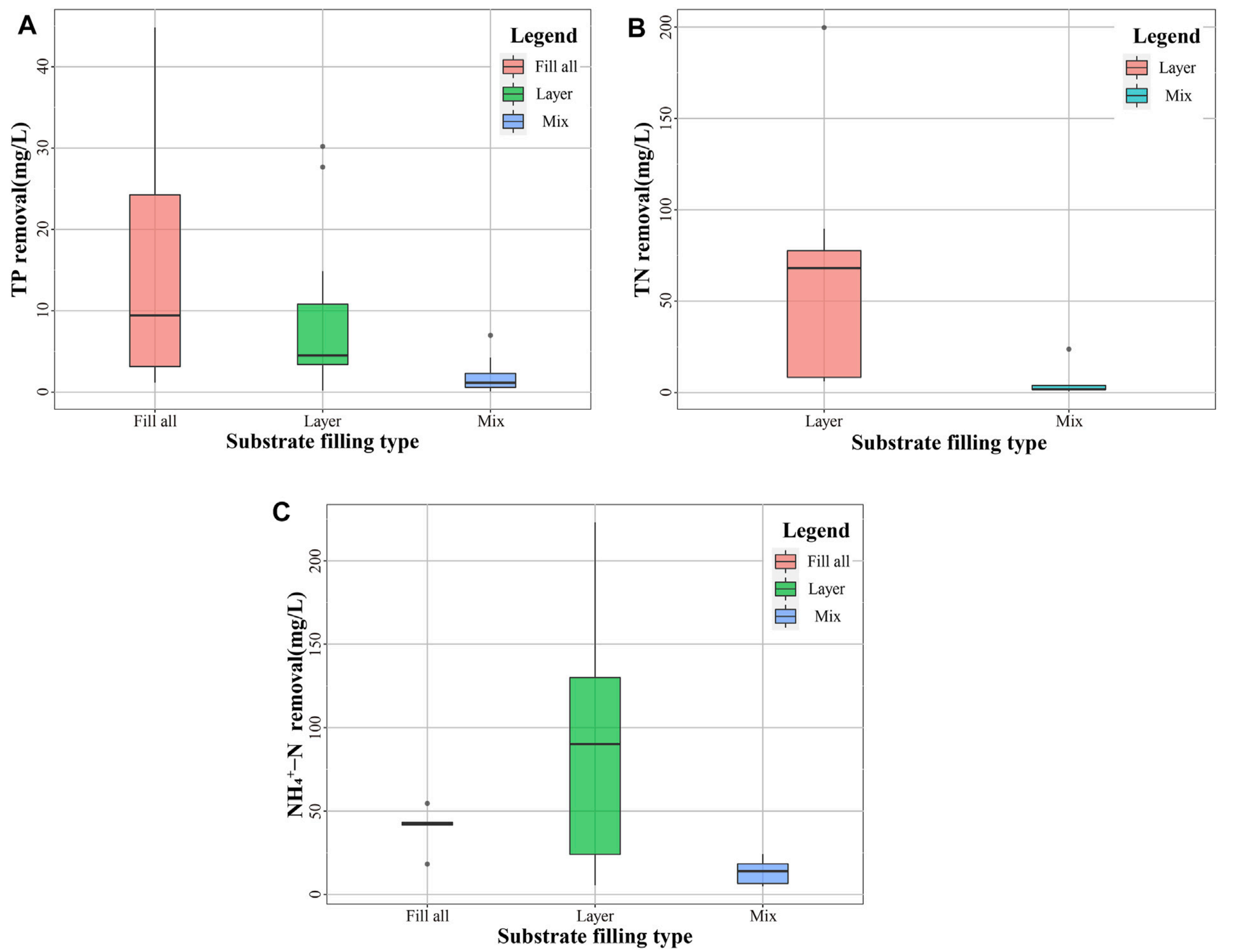

FIGURE 1 | Influence of the substrate filling mode on pollutant removal by steel slag substrate constructed wetlands (SSCWs). **(A)** total phosphorus (TP) **(B)** total nitrogen (TN) **(C)** ammonium nitrogen (NH_4^+-N) (the pictures are all original data plots, and data conversion is performed during data analysis).

(Shilton et al., 2013), secondary effluent of sewage treatment plants (Xiong et al., 2011; Zhang et al., 2015; Chen et al., 2020), polluted river waters (Shi et al., 2014; Ge et al., 2015; Ge et al., 2016), hydroponic sewage (Park et al., 2017), agricultural sewage (Lu et al., 2016; Yuan et al., 2017), dairy farm sewage (Adera et al., 2018), leachate (Saeed et al., 2020), and other sewage. Besides, SSCWs demonstrate high P recovery potential. **Table 1** summarizes the latest crucial scientific research on SSCWs, most of which were carried out on the scale of batch experiments (Baker et al., 1998; Kim et al., 2006; Blanco et al., 2016) in laboratories (Huang and He, 2011; Wu et al., 2011; Barca et al., 2014; Ren et al., 2014; Zhang et al., 2015; Ge et al., 2016; Ahmad et al., 2017). Some of the studies were conducted on a pilot scale (Hussain et al., 2015; Yun et al., 2015; Mohamed et al., 2016; Yuan et al., 2017; Chen et al., 2020; Hamdan et al., 2020), nothing in which full-scale field applications are not yet available.

Steel slag substrates stuffed in SSCWs mainly include BOF steel slag (Baker et al., 1998; Hussain et al., 2015; Blanco et al., 2016; Ge et al., 2016), electric arc furnace (EAF) steel slag (Drizo et al., 2006; Barca et al., 2013; Barca et al., 2014; Adera et al., 2018), and modified steel slag (Ahmad et al., 2017; Park et al., 2017). Due to the addition of limestone in the steelmaking process, BOF steel slag contains high concentrations of CaO and exhibits high P removal capacity (Barca et al., 2013). Therefore, in some studies, when BOF slag is rapidly cooled, the content of unstable crystalline-free CaO and the alkalinity of SSCWs will be significantly reduced (Park et al., 2016). Regarding P removal capacity, BOF steel slag performs better than EAF steel slag. However, with a low pH value and many adsorption sites, the latter can remove P not only by precipitation but also by adsorption (Ge et al., 2016).

Subsurface SSCWs are most widely used according to the flow direction and are divided into unsaturated vertical flow (Huang and He, 2011; Wu et al., 2011; Xiong et al., 2011; Shilton et al., 2013; Ren et al., 2014; Shi et al., 2014; Cui et al., 2015; Hussain et al., 2015; Zhang et al., 2015; Blanco et al., 2016; Ge et al., 2016; Lu et al., 2016; Mohamed et al., 2016; Ahmad et al., 2017; Yuan et al., 2017; Adera et al., 2018; Hamdan et al., 2020; Saeed et al., 2020) and saturated horizontal flow (Barca et al., 2013; Barca et al., 2014; Ren et al., 2014; Cui et al., 2015; Ge et al., 2015; Park et al., 2017; Yuan et al., 2017; Adera et al., 2018; Xu et al., 2019; Chen et al., 2020) SSCWs. Next, vertical flow SSCWs require only

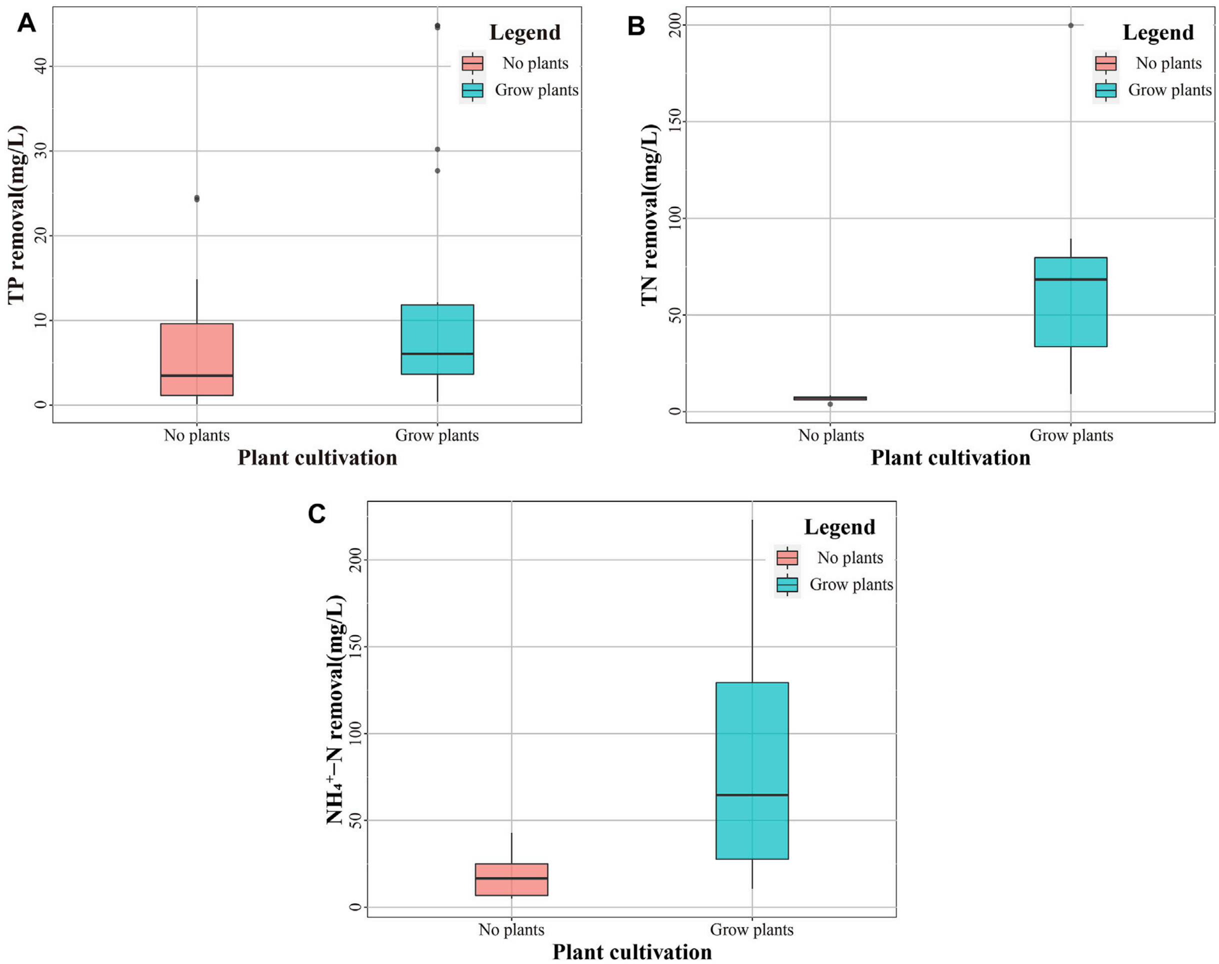

FIGURE 2 | Influence of plant cultivation on pollutant removal in SSCWs. **(A)** TP **(B)** TN **(C)** NH_4^+-N (the pictures are all original data plots, and data conversion is performed during data analysis).

a small amount of ground to operate but provide appropriate contact time and anaerobic time between water and substrate to ensure a better nitrogen and phosphorus removal performance (Yun et al., 2015). The intermittent water inflow and aeration condition (Shi X. et al., 2017) can promote the nitrification process and P transformation process. Like vertical flow SSCWs, horizontal flow SSCWs also demonstrate enough contact time to remove P in the sewage, but they require a larger amount of ground. Besides, CO_2 interference is avoided for saturated operation, and little $CaCO_3$ blockage is generated in the horizontal flow SSCWs. In addition, the alkalinity of effluent can be neutralized by spraying CO_2 on the effluent. With low cost and minimal technical requirements, horizontal flow SSCWs exhibit enough contact time to remove P in the sewage. No air entering CO_2 avoids interference, and almost no $CaCO_3$ will be generated, thereby reducing the blockage (Ren et al., 2014). However, in the light of the alkalinity of the effluent, the pH value of the sewage can be neutralized by spraying CO_2 in later stages (Park et al., 2017).

In addition, contentious issues exist regarding the pollutant removal efficiency of SSCWs. For example, one study proposed that EAF steel slag would release P when removing low P concentration sewage (Drizo et al., 2006) and believed that steel slag was not suitable for removing low P concentration sewage, which is in contrast to the results of other studies. Moreover, contradictions are found on the issue of whether the main P removal mechanism is adsorption or precipitation (Barca et al., 2014; Ge et al., 2016). In fact, the acid–base condition determines the main mechanism of P removal. Under alkaline conditions, precipitation, depending on the content of CaO in the substrate, is the main removal mechanism; thus, P can be quickly removed. In contrast, under acidic conditions, P is removed mainly by adsorption, and the removal process is slow and lasting (Ahmad et al., 2017; Xu et al., 2019). Moreover, HRT is a significant factor influencing removal efficiency. Too short HRT would result in incomplete removal of N and P, while a longer than the optimal time would lead to an unstable release of adsorbed P (Shilton et al., 2013), limited microbial growth, and

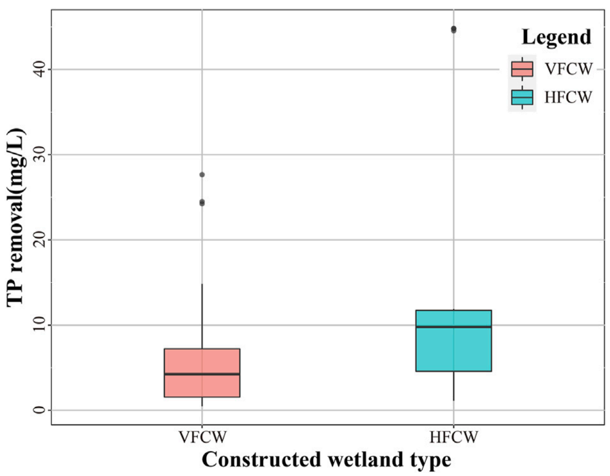

FIGURE 3 | TP removal in horizontal and vertical flow SSCWs with plant cultivation (the pictures are all original data plots, and data conversion is performed during data analysis).

increased pH value of effluent. In recent years, some studies focused on the issue of whether other pollutants in the sewage would influence P removal efficiency. On the one hand, researchers revealed that organic acids and organic colloids can block active surface sites of substrates and reduce P adsorption. On the other hand, some laboratory experiments showed that the inhibitory effect mentioned above can be mitigated over time, and eventually, P adsorption can be promoted, such as in iron oxide compounds, cations, and algae (Barca et al., 2013; Ge et al., 2016).

Significant Influence of the Substrate Filling Mode on the Nitrogen and Phosphorus Removal Capacity

The substrate filling method imposed a significant influence on the removal of TP (p = 0.001), TN (p = 0.002), and NH_4^+-N (p = 0.009) (**Figure 1**). The degree of TP removal in SSCWs with different filling modes was ordered as follows: single steel slag substrate filling (14.95 mg TP/L) > layered combined substrate filling (7.19 mg TP/L) > mixed combined substrate filling (1.95 mg TP/L) (**Figure 1A**). The main reason why the TP removal amount of combined substrate filling is significantly lower than that of single steel slag filling is that in a limited-volume CW, the introduction of other substrates can reduce the steel slag amount, resulting in a decrease in the P removal amount during the adsorption and co-precipitation process. The main reason why the TP removal amount of mixed combined substrate filling is significantly lower than that of layered combined substrate filling is that mixed combined substrates can cause the steel slag surface to be partially covered, thus reducing the number of adsorption sites, or they can impede the release of calcium ions (Shi X. et al., 2017).

Next, the pH of SSCWs filled with single steel slag can reach as high as 12.4 (Gomes et al., 2018), which is not conducive to plant growth and microbial survival. These systems lack plant root adsorption and microbial metabolic activities and only achieve a small amount of physical adsorption. Compared to single steel slag, a combined substrate composed of steel slag and other substrate materials improved N removal due to the relatively suitable environment for microorganisms and plants (Shen et al., 2020). The TN removal of SSCWs with different combined substrate filling modes was as follows: layered combined substrate filling (14.75 mg TN/L) > mixed combined substrate filling (4.38 mg TN/L) (**Figure 1B**). The NH_4^+-N removal of SSCWs with different substrate filling modes was as follows: layered combined substrate filling (87.59 mg NH_4^+-N/L) > single steel slag substrate filling (40.46 mg NH_4^+-N/L) > mixed combined substrate filling (13.44 mg NH_4^+-N/L) (**Figure 1C**). These results indicate that the different substrate filling modes exert a profound impact on the removal amounts of N and P, and layered combined substrate SSCWs exhibit a better N removal capacity. Compared to layered combined substrate filling, mixed combined substrate filling causes other substrate materials to cover the adsorption sites of the steel slag substrate, thereby reducing the adsorption capacity of the steel slag substrate (Shi P. et al., 2017). Moreover, in the layered combined SSCWs, plants are usually cultivated in the non-steel slag materials layer with a milder acid–base condition (Cui et al., 2015; Yuan et al., 2017; Zheng et al., 2021), which better promotes the de-N effect of plants and microorganisms (Lan et al., 2018).

Plant Cultivation can Improve the Simultaneous Nitrogen and Phosphorus Removal Capacity of Steel Slag Substrate Constructed Wetlands

The strong alkalinity of single steel slag is not conducive to plant survival, so plants are usually cultivated in the combined substrate SSCWs. Plant cultivation in SSCWs significantly increased the removal amounts of TP by 6.02 mg TP/L (p = 0.026), TN by 62.18 mg TN/L (p = 0.000), and NH_4^+-N by 69.16 mg NH_4^+-N/L (p = 0.000) (**Figure 2**), indicating plant cultivation can improve the simultaneous N and P removal capacity of SSCWs. The adsorption of P by plant roots helps to remove P. However, the high pH can lead to plant death and the release of P through decaying plants (Lu et al., 2021; Zheng et al., 2021); thus, generating two opposing views on whether plant cultivation can improve the simultaneous removal of N and P. Our results suggest that the P adsorbed by plant roots offsets the P released by plant death. In this way, plant cultivation can enable the SSCWs to simultaneously remove N and P with high efficiency.

Horizontal Flow (Vs. Vertical Flow) Steel Slag Substrate Constructed Wetlands Have a Higher Removal Capacity of P

The average TP removal amount in horizontal flow SSCWs was 6.38 mg TP/L larger than that in vertical flow SSCWs (**Figure 3**). In SSCWs, Ca-P deposits cover the surface of steel slag, resulting in decreased P removal. The phenomenon is more serious in

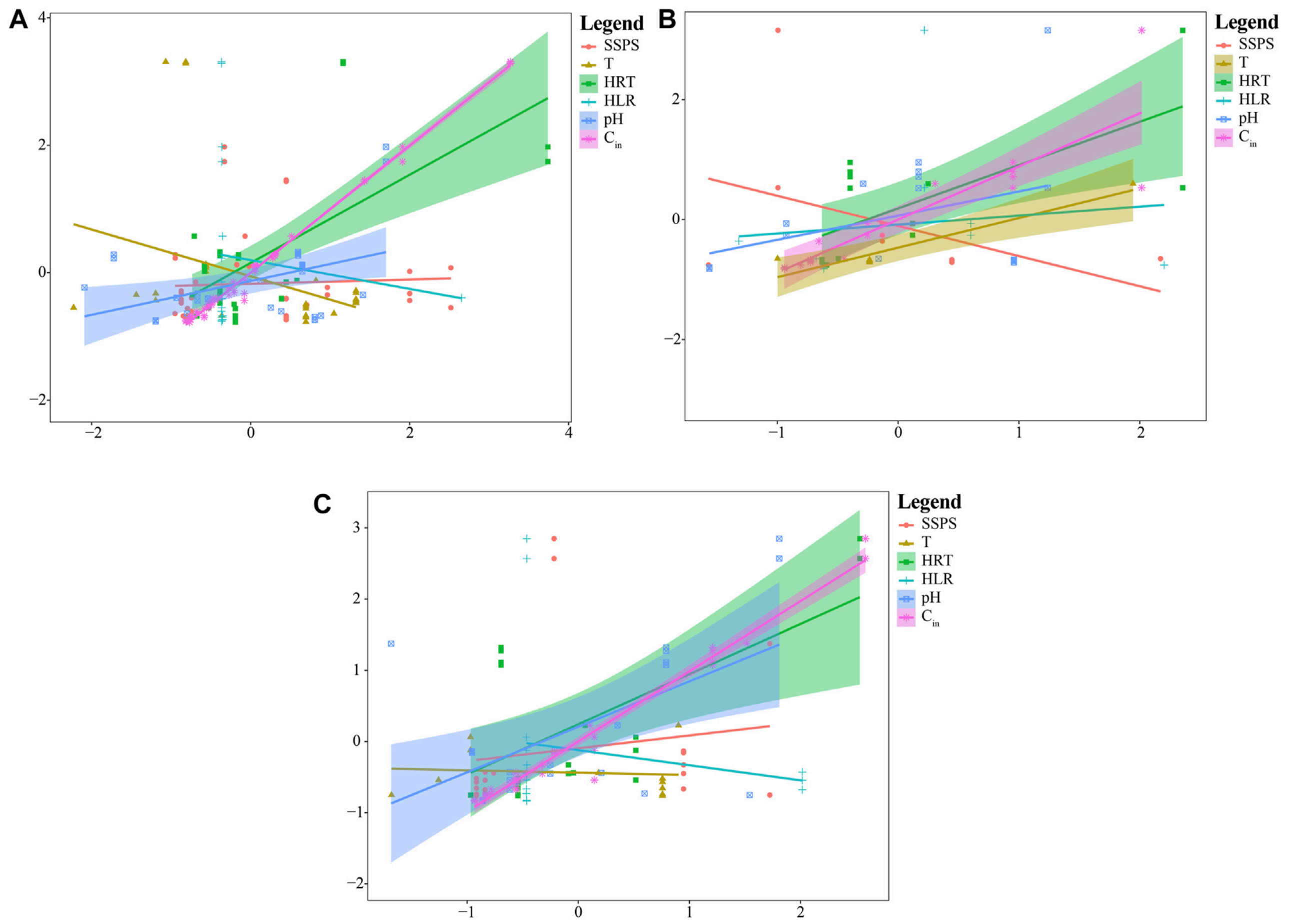

FIGURE 4 | Pearson correlation analysis scatter plot and fitting line of the pollutant removal amount and experimental parameters. The error range of the experimental parameters with $p < 0.05$ is shown in figure. **(A)** TP **(B)** TN **(C)** NH_4^+-N.

vertical SSCWs due to the frequent intermittent vertical flow transporting the deposits to the deeper substrates, then reducing the P adsorption. In contrast, the water flow remains horizontal and stable in horizontal flow SSCWs, enabling the sewage to be in full contact with steel slag, thus resulting in increased removal of P. In addition, strictly controlling the hydraulic residence time is necessary to reduce the pH while ensuring pollutant removal in horizontal flow SSCWs.

Operation Parameters of Steel Slag Substrate Constructed Wetlands Affected N and P Removal Capacity

The TP removal amount of SSCWs was positively correlated with the HRT (r = 0.643; p = 0.000), pH (r = 0.430; p = 0.010), and C_{in} (r = 0.997; p = 0.000) (**Figure 4A**). With increasing HRT, the contact time between steel slag and sewage increased, consequently increasing the reaction time, thereby improving the TP removal amount. However, an excessively long HRT could increase the pH value of the effluent. In practical applications, the HRT should be reasonably controlled. Alkaline conditions are conducive to forming Ca-P, while acidic conditions are conducive to forming Fe-P and Al-P, each less stable than Ca-P. In addition, excessively high alkalinity could lead to the release of P (Shen et al., 2020). Considering the sewage discharge standards in most countries (pH 6–9), the pH of the effluent should be stabilized below 9. The positive correlation between TP removal and C_{in} suggests that in most experiments, steel slag can release enough Ca^{2+} to form precipitation with the high concentration of PO_4^{3-} in sewage.

The TN removal amount was positively correlated with T (r = 0.943; p = 0.005), HRT (r = 0.689; p = 0.004) and C_{in} (r = 0.887; p = 0.000) (**Figure 4B**). The NH_4^+-N removal amount was positively correlated with the HRT (r = 0.624; p = 0.004), pH (r = 0.573; p = 0.005) and C_{in} (r = 0.914; p = 0.000) (**Figure 4C**). With increasing temperature, the nitrification–denitrification rate was improved, and the TN removal amount increased.

Among these operation parameters, C_{in} was the most important factor influencing N and P removal amount (p = 0.002) (**Figure 5**), followed by HRT (p = 0.002), and then, T (p = 0.004) and pH (p = 0.008) decreased sequentially and positively correlated with N and P removal amount.

In addition, based on regression analysis, we quantitatively described the relationships between the TP, TN, NH_4^+-N removal amount and the operation parameters in SSCWs.

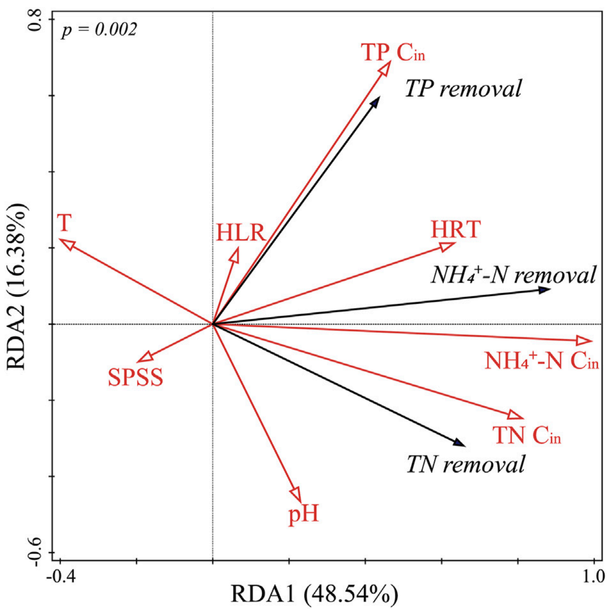

FIGURE 5 | Redundancy analysis of the influence of the operation parameters on pollutant removal.

Eqs 2–4 described the above relationships in non-plant cultivation SSCWs.

$$\Delta C_{TP} = -0.017\,SSPS + 0.998\,C_{in} \quad (r^2 = 0.995; n = 57; p = 0.000; F = 1511.000) \tag{2}$$

$$\Delta C_{TN} = 0.540\,C_{in} \quad (r^2 = 0.800; n = 19; p = 0.000; F = 8.021) \tag{3}$$

$$\Delta C_{NH_4^+-N} = -221.562 + 1.112\,SSPS + 3.832\,T + 16.121\,pH + 0.866\,C_{in} \quad (r^2 = 0.983; n = 31; p = 0.000; F = 235.000) \tag{4}$$

where $\Delta C = C_{in} - C_{out}$ denotes the TP, TN, and NH_4^+-N removal amounts (mg/L); C_{in} and C_{out} are the influent and effluent concentrations (mg/L), respectively; SSPS is the steel slag particle size (mm); T is the temperature (°C); and pH denotes the acidity or alkalinity.

Eqs 5–7 described the above relationships in plant cultivation SSCWs:

$$\Delta C_{TP} = 8.681 - 0.287\,T + 0.963\,C_{in} \quad (r^2 = 0.999; n = 27; p = 0.000; F = 2506.000) \tag{5}$$

$$\Delta C_{TN} = -391.380 + 56.980\,pH + 0.226\,C_{in} \quad (r^2 = 0.695; n = 27; p = 0.000; F = 7.585) \tag{6}$$

$$\Delta C_{NH_4^+-N} = -174.065 + 3.912\,T + 0.871\,C_{in} \quad (r_2 = 0.983; n = 27; p = 0.000; F = 190.400) \tag{7}$$

where $\Delta C = C_{in} - C_{out}$ denotes the TP, TN, and NH_4^+-N removal amounts (mg/L); C_{in} and C_{out} are the influent and effluent concentrations (mg/L), respectively; T is the temperature (°C); and pH denotes the acidity or alkalinity.

Eqs 2 and **4**, **5**, and **7** indicate that plant cultivation weakens the dependence of SSCWs on SSPS for P and NH_4^+-N removal. Compared to non-plant cultivation SSCWS, temperature is one of the determinants of P removal in plant cultivation SSCWs.

CONCLUSION

Our results indicate that layered combined substrates can significantly increase the TN and NH_4^+-N removal amounts in SSCWs but reduce the TP removal amount. Plant cultivation in combined substrate SSCWs can compensate for the decline in TP removal. Compared with vertical flow, horizontal flow SSCWs demonstrate a higher removal capacity of P. Next, T, HRT, pH, and C_{in} significantly affected the N and P removal capacity of SSCWs. To conclude, plant cultivation and combined substrates can improve the simultaneous removal of N and P in SSCWs. This study can serve as a reference to solve certain problems encountered in SSCWs.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/Supplementary material, and further inquiries can be directed to the corresponding author.

AUTHOR CONTRIBUTIONS

JZ: Data curation and analysis, writing—original draft. YZ: Aided in interpreting the results and worked on the manuscript. XY: Worked on the technical details, supervised the findings of the work and helped in the development of manuscript. SD: Writing—review and editing. JY: Data curation. YM: Data curation.

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