

Optimised phosphorus removal technology for small-scale wastewater treatment by combining metallurgical slags

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Abstract

Different ways of combining argon oxygen decarburisation slag (AOD) or electric arc furnace slag (EAF) with blast furnace slag (BFS) for achieving better phosphorus (P) removal performance in small-scale wastewater systems (SSWSs) were examined. The three types of slag were combined in varying mass ratios and with different dosing procedures in batch experiments using synthetic solution and real wastewater. The results showed that within 4 h, 0.5 g BFS and AOD with mass ratio (g:g) 0.15:0.35, added simultaneously, removed 97.4% of P from 100 mL synthetic solution containing 21.48 mg P L⁻¹. Moreover, AOD combined with BFS in mass ratio 1.5:0.5 or 1:1 and at a dose of 20 g L⁻¹ achieved better P removal (>93.0%) than either of the two slags alone at the same dosage (around 84.0%) or at a higher dosage of 25 g L⁻¹ (91.6%). However, combining BFS and EAF gave no significant improvement in P removal performance compared with using either type of slag alone. Polynomial regression analyses revealed a significant relationship between supernatant final pH and P removal, with an R² value of 0.996 and 0.882 for wastewater and synthetic solution, respectively, when only data with pH >8 were used.

Keywords

BFS; EAF; AOD; phosphate removal; slag combination

Introduction

Around 700,000 households in Sweden are connected to small-scale wastewater systems (SSWSs) such as septic tanks followed with sand filter, soil infiltration systems or constructed wetland systems (Johansson Westholm, 2006; Naturvårdsverket, 2014). It has been estimated that the SSWSs in Sweden released around 290 tons of phosphorus (P) in 2009, due to the inadequate P removal of these systems (Naturvårdsverket, 2014). This kind of P release contributes a significant share of the P load to water bodies with limited water exchange, such as Swedish lakes and the Baltic Sea. In many other countries such as Japan and China, the primary type of SSWS in rural areas is the septic tank (Mizuochi et al.; Liang et al., 2010). According to Abegglen et al. (2008), septic tank and sand filter have very low P removal efficiency, fluctuating around 10%. Hence sequential technology for P removal is necessary to improve the P removal performance and mitigate eutrophication in receiving water bodies.

Typical technologies for P removal from small-scale domestic wastewater systems include filtration (Johansson Westholm, 2006). Compared with biological P removal involving P consumption by bacterial reproduction in the wastewater or chemical P removal by adding aluminium or iron as flocculants that bind the dissolved P, filtration is a simpler technology that requires less maintenance. Therefore it is better suited for P removal from small-scale household wastewater systems (Shilton et al., 2006; Gustafsson et al., 2008). The spent material can be used as a P fertiliser and soil conditioner (Hylander et al., 2005), which is a beneficial feature as SSWSs are usually located in rural areas in need of these products.

Metallurgical slag from the steel-making industry has been identified as a potential P removal material for SSWs, as it is efficient in P removal, widely available and cheap (Johansson Westholm, 2006; Gustafsson et al., 2008). The satisfactory P removal ability of slag is attributable to the high content of calcium silicates, free lime and iron and aluminium oxides (Eveborn et al., 2009; Claveau-Mallet et al., 2012; Zuo et al., 2015; Han et al., 2016). However, the P removal performance varies from one type of slag to another. Research has shown that electric arc furnace slag (EAF) and argon oxygen decarburisation slag (AOD) can achieve better P removal than blast furnace slag (BFS), owing to the resulting higher pH of the wastewater solution (Gustafsson et al., 2008; Claveau-Mallet et al., 2012; Zuo et al., 2015). In a recent study where the pH of synthetic wastewater was increased from 4.5 to 8.72, the P removal rate of basic oxygen furnace slag (BOF) was found to increase gradually, with the P removal mechanism involved shifting from adsorption on iron oxides to weak adsorption accompanied by Ca-P precipitation (Han et al., 2016).

It has also been observed that after being in contact with wastewater for a period, EAF slag particles tend to clump together due to their pozzolanic nature, while this was not observed in spent BFS in our previous research (manuscript under review). Therefore, a combination of EAF and BFS was tested, based on the assumption that this could prevent clumping of spent slag particles and facilitate the P recycling process. In experiments with both real wastewater and synthetic wastewater solution, the P removal performance of three types of slag (BFS, EAF and AOD) was examined. BFS was combined with both EAF and AOD, with the aim of achieving better P removal performance, in combinations denoted BFS+EAF and BFS+AOD. The effect of mass ratio (g:g) and slag dosing procedure (timing) on P removal was also investigated in order to optimise the technology for P purification.

It has been reported previously that pH is a significant factor influencing P removal from wastewater (Claveau-Mallet et al., 2012; Han et al., 2016). The relationship between supernatant final pH and P removal was therefore also investigated, in an attempt to establish a quick and easy on-site way to indicate P removal.

MATERIALS AND METHODS

Materials

The three types of slag used were produced in Sweden. BFS slag was provided by Merox AB, Oxelösund, AOD slag by Outokumpu Stainless AB, and EAF slag by Höganäs AB. The particle size of all three types of slag was approximately 1.0-2.4 mm. Since the slag samples were stored in the laboratory for more than 10 months before use, they were activated by heating in a muffle oven at 1000 °C for 15 min one day before being added to the wastewater to alleviate the effect of ageing on P removal performance. Chemical characterisation of the AOD and EAF was performed by XRD analysis, while data on the chemical composition of BFS were taken from the literature (Johansson Westholm, 2010).

Table 1. Chemical composition of slag samples (mg g⁻¹)

	Si	Mn	Cr	Ni	Al	Ca	Fe	Mg
AOD	149.8	3.9	10.3	0.47	9	380	3	33
BFS	158.6	4.6	nv	nv	68.8	214.3	3.7	100.8
EAF	162.4	11.6	33	0.39	21.7	325	3	50.1

nv, no value available.

Synthetic solution with an initial P concentration of 21.5 mg L⁻¹ was used in the batch experiments. It was prepared fresh daily by dissolving KH₂PO₄ in deionised water. The synthetic solution had an

ionic background of 0.001 mol L⁻¹ NaNO₃, achieved by adding a fixed volume of 0.1 mol L⁻¹ NaNO₃. The pH of the synthetic solution was around 5.6. Since the slag types used are known to be highly alkaline, no pH adjustment was made to the synthetic solution in order to conserve resources.

Real wastewater was collected from a septic tank with design flow 1.6 m³ d⁻¹. Apart from filtering through cotton to remove the coarse particles, no further treatment of the real wastewater was conducted. It was stored in plastic containers at room temperature for less than five days, during which there were negligible changes in pH and P concentration according to analysis of samples taken before and after the experiment. The P concentration was 21.89 mg L⁻¹ and the pH was 8.16.

Experimental methods

Effect of mass ratio on P removal. The three types of slag were combined in two pairs with three different mass ratios (Table 2). The slag pairs were then tested by adding a dose of 0.5 g to 100 mL synthetic solution or real wastewater in plastic bottles, placing the bottles in an end-over-end shaker and shaking for 24 h at 50 rpm and room temperature. The three types of slag were also tested separately, as a control group, by adding 0.5 g of each slag to 100 mL synthetic solution or wastewater and shaking as described for 24 h. Supernatant was sampled for pH and P analysis in all cases.

Table 2. Mass ratios of the two slag pairs

	Pair I		Pair II	
	BFS (g)	AOD (g)	BFS (g)	EAF (g)
Mass ratio a	0.15	0.35	0.15	0.35
Mass ratio b	0.25	0.25	0.25	0.25
Mass ratio c	0.35	0.15	0.35	0.15

Effect of dosing procedure on P removal. Previous research has shown that the release of hazardous metals from the slag material to the treated wastewater increases with contact time (Engström et al., 2014). Therefore the effect of dose timing on P removal was tested in a series of batch experiments in which a 0.5 g dose of the different slag samples was added to 100 mL synthetic solution according to two dosing procedures: a) first dose of 0.15 g BFS to the solution, followed two hours later by 0.35 g AOD or EAF; B) combined dose of 0.15 g BFS and 0.35 g AOD or EAF simultaneously at the beginning of the experiment. All suspensions were shaken end-over-end at 50 rpm for 4 h. A control experiment was conducted by adding 0.35 g BFS, 0.15 g EAF and 0.15 g AOD to 100 mL synthetic solution. Supernatant was sampled every two hours to determine the P removal and pH in all cases.

Effect of dose and mass ratio on P removal from real wastewater. In addition to the mass ratios listed in Table 2, mass ratios (g: g) of 0:2.5, 0.5:1, 1:1, 0.5:1.5 and 0.5:2 were tested in order to identify an optimal dose and mass ratio for P removal from real wastewater: The slag samples were added to 100 mL real wastewater, shaken end-over-end for 8 h and the supernatant was sampled for analysis of pH and P removal.

Analytical methods

For all batch experiments, the bottles were kept still for 2 min to allow particle settling prior to supernatant sampling. The pH of the supernatant was measured immediately after sampling using a Hach pH meter (SensionTM pH31) with a typical combination electrode. The samples were then filtered with a 0.45 µm syringe filter before being stored in the freezer prior to P analysis. A Seal Analytical AA3 Autoanalyzer was employed to analyse the phosphate P (PO₄-P) concentration.

Prior to these analyses, the instrument was calibrated with five working standard solutions in the range 0-20 mg P L⁻¹.

The relationship between final pH of the supernatant and P removal was analysed using the software IBM SPSS Statistics 23. Regression analysis was performed to determine the correlation of P removal with final supernatant pH for both synthetic solution and wastewater (Nilsson et al., 2013).

RESULTS AND DISCUSSION

Effect of mass ratio on P removal. Phosphorus removal from the synthetic solution was much better than from the real wastewater in all cases, irrespective of the slag combination and the mass ratio tested (Figure 1). More than 70% P removal was achieved for the synthetic solution, while for the real wastewater P removal was less than 50%. The rate of P removal from synthetic solution was higher than 99.0% for the slag pair BFS+AOD at all mass ratios tested. Both slag pairs achieved better P removal from wastewater when the mass ratio was 0.15:0.35 compared with the other two mass ratios tested. However, being combined with BFS did not enhance the P removal of AOD or EAF, as these two types of slag showed better performance when they were added alone to either synthetic solution or real wastewater in this experiment.

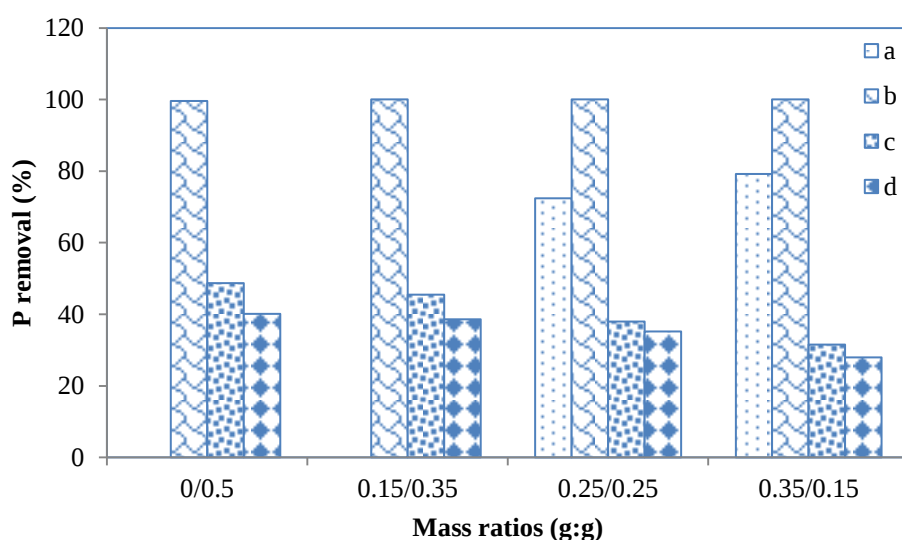


Figure 1. Effect of mass ratio on phosphorus (P) removal rate: a: BFS with EAF in synthetic solution; b: BFS with AOD in synthetic solution; c: BFS with AOD in wastewater; d: BFS with EAF in wastewater.

Effect of dosing procedure on P removal. The combination BFS+AOD achieved very satisfactory P removal (97.35%) within 4 h for the procedure with both types of slag dosed simultaneously (Figure 2). For the procedure with AOD added 2 h after BFS, the P removal was initially 91.93%, i.e. slightly lower than when both were added together. But on addition of AOD 2 h later the P removal almost tripled, from 33.1% to 91.9%. This result was not surprising, as AOD exhibited superior P removal performance to BFS and EAF, with a dose of 0.15 g achieving 97.9% P removal from 100 mL synthetic solution.

The two dosing procedures had the opposite effect on the combination of BFS with EAF (Figure 2). When the two types of slag were added at the same time, the P removal was actually lowered from 49.7% to 47.39%. With the procedure where EAF was added 2 h later than BFS, the P removal increased from 33.1% in the first 2 h to 52.4% after 4 h. Although the pH of the synthetic solution

with BFS+EAF added increased from 9.29 to 9.59 between 2 and 4 h, P removal rate decreased, suggesting that some of the captured P was released to the synthetic solution.

Analysis of the concentrations of hazardous metals (e.g. Cr, Zn, Pb) in the supernatant by ICP-OES revealed release of Cr^{3+} in the wastewater with added EAF on the first day, but not in the wastewater with added AOD (data not shown). Therefore the procedure with BFS and AOD added simultaneously can be recommended for P removal in SSWSs, as no increased risk of leaching hazardous metals would be expected.

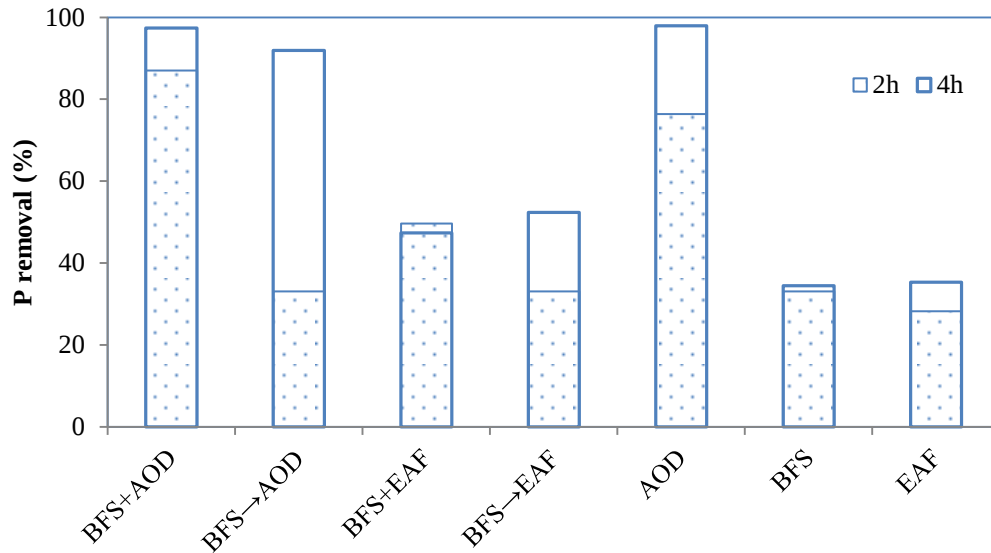


Figure 2. Effect of dosing procedure on P removal. BFS+AOD, BFS+EAF: both dosed simultaneously. BFS→AOD, BFS→EAF: the other slag dosed 2 h after BFS. AOD, BFS and EAF: added alone.

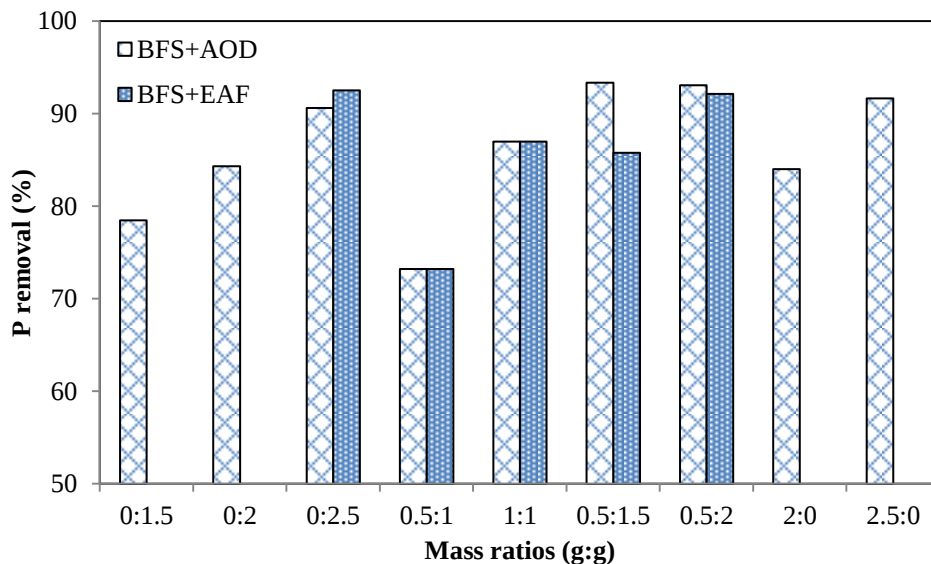


Figure 3. Effect of varying doses and mass ratio on P removal rate.

Effect of dose and mass ratio on P removal from real wastewater. The P removal rate varied when BFS+AOD and BFS+EAF were added in different doses and mass ratios (Figure 3). The best P removal (93.3%) was achieved by BFS+AOD with mass ratio (g:g) 0.5:1.5, indicating that the P removal was enhanced when the two types of slag were combined in this ratio. A positive relationship between the dose of AOD alone and P removal rate was observed (see first three bars in

Figure 3). As the AOD dose increased from 1.5 g to 2.5 g in 100 mL wastewater, the P removal increased gradually from 78.5% to 90.6%. However, no increase in P removal was observed for BFS+AOD when the dose and mass ratio changed from 0.5:1.5 to 0.5:2.

The combination BFS+EAF did not have any great influence on P removal compared with the combination BFS+AOD. EAF showed its best P removal performance when added alone to 100 mL wastewater in a dose of 2.5 g. It is worth noting that when the dose and mass ratio of BFS+EAF increased from 0.5:1 to 1:1, a significant increase in P removal from 73.2% to 87.0% was observed.

In conclusion, the combination BFS+AOD with mass ratio 0.5:1.5 at a dose of 20 g L⁻¹ and a hydraulic retention time of 8 h can be suggested for treating wastewater from a septic tank.

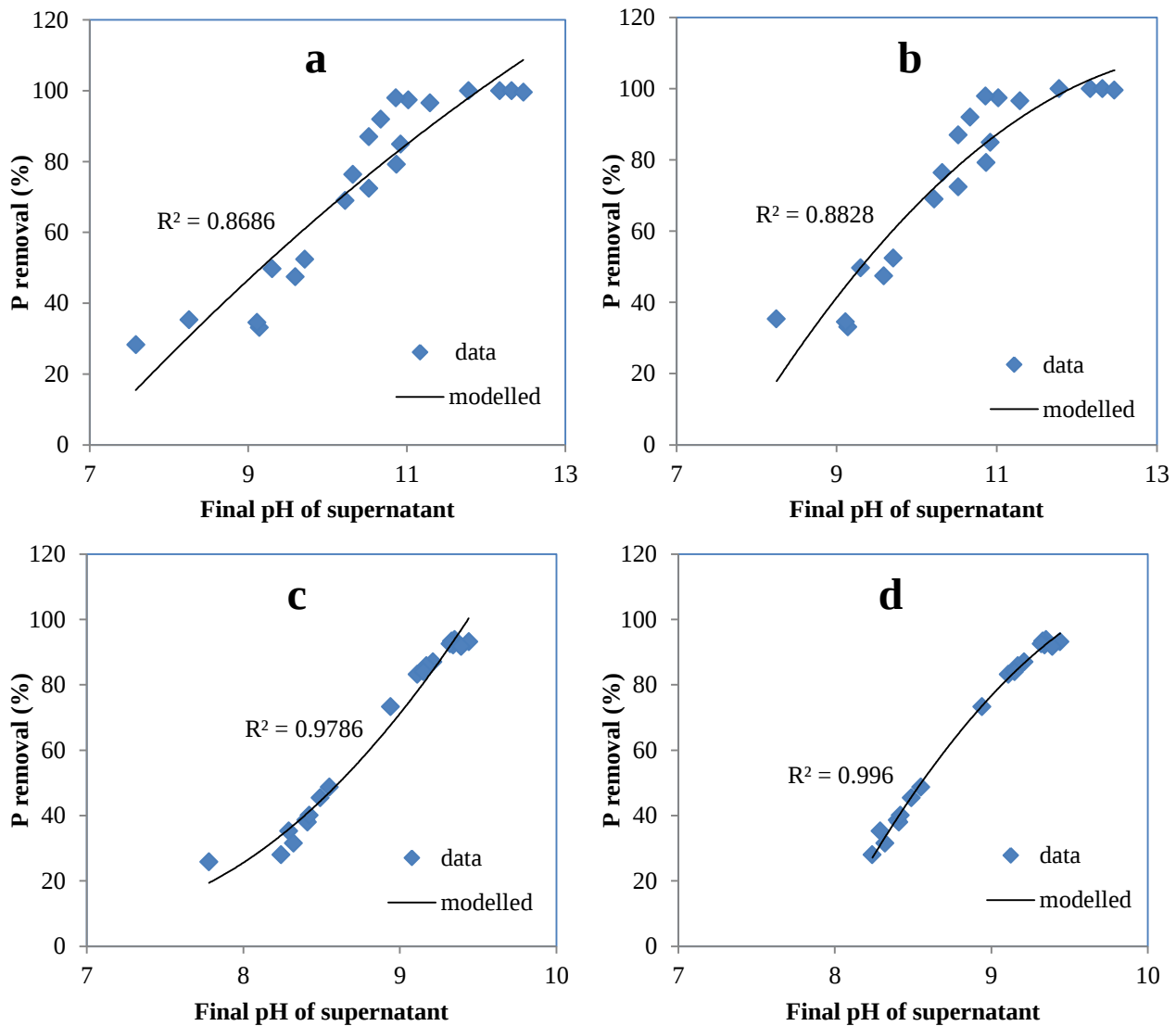


Figure 4. Correlation between final pH of supernatant and P removal. a) All data for the synthetic solution; b) data for synthetic solution samples with pH > 8; c) all data for the real wastewater; d) data for wastewater samples with pH > 8.

Correlation between pH and P removal. Both linear and non-linear regression analysis on P removal from sythetic solution and real wastewater was conducted. A polynominal relationship with an order of two between supernatant final pH and P removal was found (Figure 4). The R²

value indicated that 86.86% of the variation was explained by the model for synthetic solution. The R^2 value was not improved greatly by deleting data with $\text{pH} < 8$.

In an unexpected finding, the R^2 value was higher for the real wastewater data than for the synthetic solution data. The R^2 squared for wastewater data was 0.9786, and was even closer to 1 ($R^2 = 0.996$) when values at $\text{pH} < 8$ were omitted. It has been reported previously that the presence of organic matter and bicarbonates can significantly inhibit P removal (Song et al., 2006; Nilsson et al., 2013). The organic matter and bicarbonates probably act as a pH buffer in the wastewater, influencing P removal indirectly. Based on the good fit between the experimental data and the model, it is possible that the pH of the effluent can be used as an indicator of P removal in SSWSs filled with slag materials. Determination of the relationship between effluent pH and P removal would be very beneficial in SSWS management, since in rural areas access to laboratory instruments for P determination is usually limited.

CONCLUSION

Laboratory batch experiments with the three types of slag showed that:

1. Combining BFS with AOD enhanced the P removal performance of these two types of slag. The recommended dose of the two types of slag for 100 mL wastewater is 2.0 g with mass ratio 0.5:1.5. Satisfactory P removal (93.3%) was achieved when BFS and AOD were added simultaneously and remained in contact with the wastewater for 8 h.
2. No significant P removal enhancement was observed on combining BFS with EAF. EAF was found to be more effective when used alone at a dose of 2.5 g for 100 mL wastewater, achieving P removal of 92.5% after contact with wastewater for 8 h.
3. Final pH of the effluent could be used as an indicator of P removal from SSWSs using slag as a P treatment material. A high R^2 value (0.996) was achieved for wastewater data with $\text{pH} > 8$.

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