Effect of Waste Iron Scraps in the Removal of Total Phosphorus for Sewage Effluent

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Abstract

Background/Objectives: Total phosphorus (T-P) in effluents from sewage treatment plants (STP) causes the eutrophication of natural water. In nature, metal iron (Fe) can be oxidized to Fe^{2+} or Fe^{3+} oxidation states as well as combine with PO_4^{3-} to produce the compound $FePO_4$.

Method/Statistical analysis: The process parameters for T-P removal efficiency was investigated using iron scrap filters on STP effluents.

Finding: The results revealed the removal efficiencies of T-P and PO_4^{3-} were decreased as the filtration velocity was increased. At the condition of filtration velocity of 300m/d, T-P concentration and color intensity were suited to South Korea's water quality regulation standard of 0.2 mg/L.

Improvement/Applications: This filtration system can be used to small capacity waste water treatment plant, operation concerns and cost-benefits.

Keywords: Sewage effluent, Total phosphorus, Iron scrap, Media, Filtration, Backwashing

1. Introduction

Recent domestic climate changes - intense droughts and flooding have caused proper water provision for standard living, industries, and agriculture have not been enough. These circumstances can threaten the safety and cleanliness of the environment and cause significant economic damage. Currently, studies are focused on the surface water to establish measures aimed to secure and supply the water resources[1]. The water resources are secured using dam-like artificial structures, caused an increase in water temperature. This led to eutrophication to occur in early summer, which has become a big social problem. Recently, the regulation of T-P concentration of the effluent sewer to maintain under the standard 0.2mg/L has been strongly reinforced. Phosphorus is an essential element for human, animal and plant. Orthophosphate is the only form of P that autotrophs can assimilate.

Various methods are researched to establish stable and higher efficient means to remove T-P[2]. Factors like livestock wastewater, fertilizers found in surface water nearby agricultural lands, and existing T-P found in sewer and wastewater treatments are known to cause eutrophication of the natural water system[3].

The main methods for T-P removal are classified as such: physical-chemical treatment, electrolysis, and biological treatment. Among them, the AI- and Fe-based coagulants are used to increase efficiencies and confidence in T-P removal[4]. Continuous injection of coagulant factors generates high levels of sludge, which reduces economic feasibility; this is a drawback compared to the biological treatment[5]. The advantages of biological treatment are the processing costs are low and sludge generation is low. The drawback, however, is that there is a limit to how much phosphorus amount can be processed. The removal limit of total phosphorus by biological treatment processing is 1mg/L generally[6]. In Korea, nonpoint source pollution exists widespread nationally. The high performance sewage water treatment is not sufficient enough that performing physical-chemical treatment would be more effective than the biological treatment.

Electrochemical removal methods include performing electrolysis on the Fe and AI emitted from the electrolyzer's oxidation and reduction electrodes[7]. Once the Fe and AI ions are eluted, they combine with PO_4^{-3} and generate precipitants using electrochemical methods[4]. Such meth- ods are easy to operate and the voltage (V) of the eluted metallic ions can be easily controlled. Here, when the excess eluted Fe and AI ions are in neutral pH, the surrounding precipitates $FePO_4$ and $AlPO_4$ can be easily removed, which then allows for the removal of PO_4^{-3} in waste water [8]. However, the disadvantage to this method is that coagulant consumption levels are high, which then generates high amounts of sludge. In terms of costs, high molecular weight coagulation factor have no competitor[9]. Consequently, the optimum dose of coagulant is difficult to meet when removing the T-P. Using excessive amounts of coagulant can cause the water quality to degenerate. The oyster shells and a nonmetallic mineral combination has been used as and adsorbent to remove T-P in sewage system[10].

The study aimed to develop mitigation facility has been done in

utilizing iron scraps using filtering equipment. The iron scraps generated during iron manufacturing processes at the iron foundry. Iron can react with other oxidants, emulsifiers, carbonates, etc, and easily create iron compounds. In waste water, iron can naturally be oxidized and eluted as Fe^{2+} and Fe^{3+}, or it can combine with PO_4^{3-} or (OH^-) and become an adsorbent that facilitates precipitation[9]. Based on the influent and effluent in sewage water, the characteristics of T-P removal was investigated by operating factors to improve water quality using the filtration columns containing waste iron scraps.

2. Materials and Methods

The effluent water of STP(Sewage Treatment Plant) was supplied in Seosan city Korea. The wastewater was treated by the Cilium Nutrient Removal (CNR) process. The daily throughput is 280m³/day. The average T-P concentration of the effluent is 0.7±0.18mg/L, as shown in Table 1. To determine the T-P removal efficiency of the waste iron scraps, the influent and effluent flows of the filtration were separately collected. The color intensity emitted out of the filtration column were analyzed using Colorimeter (DR 2100AN, HACH, USA). Then, the T-P and PO_4^{3-}P were analyzed the Standard Method[11]. The energy dispersive X-ray spectrometer (NS7. FEI, America) is used to determine the elemental composition of the iron scraps. Table. 2 shows the parameters of the iron scrap. The iron scraps used in this study was waste iron scraps , which are the by-products of iron manufacture.

Table 1. : Characteristics of raw water

Parameter	Plant influent		Plant effluent	
	Range	Average	Range	Average
T-P(mg/L)	5.7-7.5	6.6±0.58	0.5-1.0	0.7± 0.18
PO₄²⁻(mg/L)	3.7-5.8	4.6±0.64	0.4-0.7	0.4± 0.11
pH	7.3-7.8	7.5±0.17	6.9-7.4	7.2± 0.12

Table 2 . Elemental compositions of iron scrap by EDS

Element(%)								
Fe	Ni	Mg	Cl	Al	Ca	Cr	Si	Cu
74	14	3	2	2	2	1	2	1

The iron scraps were washed and then treated at 500℃ for 30min to remove cutting oil on the iron's surface. The elemental composition of the iron scraps after pretreatment iron was measured using EDS (Energy Dispersive X-ray spectrometer). The results are shown that the iron scraps are almost pure of iron in Table 2. The filtration column in this investigation is shown in Figure 1. The reaction column was constructed by a cylindrical acrylic container, where the inlet was at the reactor's bottom end and the outlet was at the top end.
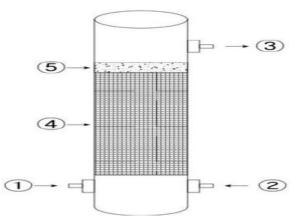

Figure 1.: Schematic diagram of filtration column (① inlet ② backwashing inlet)

The iron scraps were added into sizes smaller than 10 mm. Air and injection valves were installed at the lower end of the column for backwashing purposes. The water permeable sponges was located at the upper end of the iron scraps, which were inserted to prevent the grainy compounds (that reacted with iron scraps) from washing. The height and inflow rate values of waste iron scraps were changed in order to find the optimum the scrap's height requirement and reaction time. The detail specifications of column and experimental conditions were shown in figure. 1 and Table 3.

Table.3.: Column specifications and experiment

Parameter		Specifications		
Volume(m³)		0.047(D:0.2m/H1.5m)		
Filtration Velocity(m/day)		100~500		
Q(m³/day)			3`15	
Media height(m)		0.4	0.6	0.8
Iron scrap weight(g)		400	600	770
Back washing	Air (L/min)	20	40	60
	Water (L/min)	10	20	

3. Results and Discussion

In order to tested the removal efficiency of T-P using iron scrap filtration column, experiment were conducted with high concentration(influent waste water) and low concentration (effluent waste water), when the iron scrap height was 80cm. After 24 hours operation, sample was measured T-P removal efficiency and color intensity in terms of filtration velocity. At high concentration, influent average concentration of T-P and PO_4^{3-}P were 6.6mg/L and 4.6mg/L, respectively. And low concentration influent average concentration of T-P and PO_4^{3-}P were 0.7mg/L and 0.4mg/L. The experiment results showed in Figure 2 . When the filtration velocity was increasesd in both influent and effluent, the T-P and PO_4^{3-}P concentrations were also increased
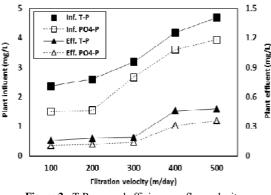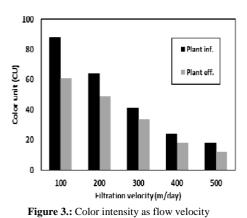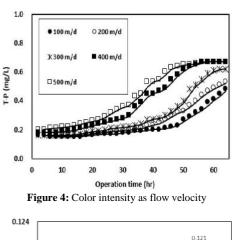

Figure 2:. T-P removal efficiency as flow velocity

To meet the released regulatory concentration 0.2 mg/L for water quality discharge standard of T-P in Korea, this iron scrap filtration system was applied in effluent(low concentration) at the small STP system. The result of color intensity after 24 hours operation was shown Figure. 3. The increased flow rate resulted in the decreasing the color intensity. The reason for this result was due to the longer contact time with iron scrap. The color intensity of domestic water quality standard dose not exceed 200 °. In case where the color is too high this causes aesthetic discomfort which can bring about civil complaints, and with the decrease in transparency can further reduce self-purification capacity of lake and river stream. Also, while the color satisfy the effluent standard levels in every conditions, low color levels are also being studied from the aesthetic point of view. Together with the T-P removal efficiency and color intensity, the filtration flow velocity can be determined as 300m/day.

To investigate the variation of T-P with operation time, the filtration test was conducted. The results are shown in Figure. 4.

As the operation time increased, the T-P concentration gradually increased first, and then increased rapidly from 30 hours. As shown in Figure.4,
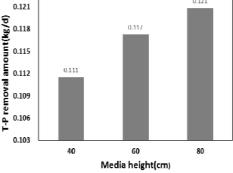

Figure 3.: Color intensity as flow velocity

Figure 4: Color intensity as flow velocity

Figure 5.: T-P removal amount in terms of media height

The T-P removal test was performed by varying height of the filtration column. The conditions of the tests were filtration rate of 300m/day and column heights of 40, 60 and 80 cm. Sample were taken for 24 hours at the intervals of 1 hour. In order to derive accurate test results, it was operated in 3 cycles and the average result was calculated. Based on the results, as the media height increased from 40cm to 80cm as shown in Figure. 5, the removal efficiency efficiency increased from 68.6%(0.22mg/L) to 74.3%(0.18mg/L). As the column's height increases, the response and contact time become important elements/requirements. In order to meet the standard regulation of less than 0.2mg/L T-P levels, the iron scraps' height need to be at minimum of 60 cm. Optimal condition for removal of T-P and color were at 60-80cm media height, 30 hours operation time and 300m/day**.**

The mechanism of oxidation and reduction of T-P removal by iron scrap in sewage filtration may be expressed as reaction (1) to (6) [7]. Major species present in surface are $FePO_4$, $Fe_3(PO_4)_2$, $Fe(OH)y(PO_4)_3$, $Fe(OH)_2$, $Fe(OH)_3$. Either Fe+3 or F+3 forms stable compound with $PO4^{-3}$ and acts as a corrosion inhibitor. The

stable compound onto the iron scrap may be responsible for decreasing the content of T-P concentration in water[12].

Fe oxidation reaction

$$Fe + 2e^- \rightarrow Fe^{2+} \tag{1}$$

$$Fe + e^- \rightarrow Fe^{3+} \tag{2}$$

Phosphorus removal reaction

$$Fe^{3+} + HPO_4^{2-} \rightarrow FePO_4 + \tag{3}$$

$$3Fe^{3+} + 2PO_4^{3-} + H_2O \tag{4}$$

$$\rightarrow Fe(OH)_3(PO_4)_2 + 3H^+$$

$$3Fe^{2+} + 2HPO_4^2 \tag{5}$$

$$\rightarrow Fe_3(PO_4)_2 + 2H^+$$

Total reaction

$$4Fe^{3+} + 3Fe^{2+} + 2PO_4^{3-} + 3HPO_4^{2-} \rightarrow FePO_4 + Fe(OH)_3(PO_4)_2 + Fe_3(PO_4)_2 + 6H^+ \tag{6}$$
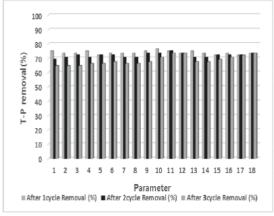
Table. 4: Backwashing process conditions

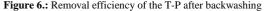|	Backwashing time (min)	Air (L/min)	Water (L/min)
1	4	20	-
2	7	20	-
3	4	40	-
4	7	40	-
5	4	60	-
6	7	60	-
7	4	20	10
8	7	20	10
9	4	40	10
10	7	40	10
11	4	60	10
12	7	260	10
13	4	60	20
14	7	20	20
15	4	40	20
16	7	40	20
17	4	60	20
18	7	60	20

The PO_4-P can easily adsorb into the interior of the sewage using the waste iron oxides, and the precipitated inorganic substances can be recycled as phosphates[10]. The surface precipitate may result either by formation of the species in solution with subsequent adsorption in iron scrap. The back washing process to removes the by-products of the loosemed produced by oxidation-reduction reactions. Three cycles of backwashing were repeatedly conducted in the process to observe the waste iron scraps recovery ability from the oxidation-reduction reactions.

Back washing processcondition were performed such that treated water and effluent were stored in a storage tank so that they could be injected with T-P concentration of the same concentration . The T-P of storage tank was measured to be 0.68 mg/L. The conditions were fixed with filtration velocity of 300m/day and iron scraps' height was 80 cm. In addition, a large amount of Fe3+ was asorbed, the filtration velocity was 30m/day, and the height of the iron scrap was 80 cm. The two backwash process were applied and compared. The first backwashing condition was air used only air and the second used air and treatment water at the same.. The experimental conditions for backwash are shown in Table 4

Backwashing was conducted for one day after the experiment. The effluent T-P concentration after backwashing were measured at 1 hour intervals. As shown in Figure. 6 and Figure. 7, the backwashing air only were shown that the removal efficiency did not recover for both the 4 minute and 7 minute. These results suggest that the byproducts adhesived to the surface of the iron scarp can not be fully desorbed during the backwashing process

and effect to the next operations. Also, at 20L/min for the air cleaning, the removal efficiency did not recover regardless of processed amounts. In order to maintain the throughput efficiency, the backwash conditions at 7 minute need the processing level of 40 L/min air + over 10L/min treatment. At 60L/min air + 10L/m treatment conditions, the removal efficiency at 4 min and 7 min were recovered
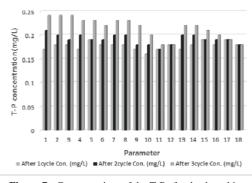

Figure 6.: Removal efficiency of the T-P after backwashing

Figure 7.: Concentration of the T-P after backwashing

In this study, the deduced backwash times are applied and continuous backwashing appeared to have positive influence on the recovery of removal efficiency, opening up the future possibilities for continuous operations.In conclusion, in using the waste iron scraps from iron manufacturing, the study showed that the local regulation for T-P removal can be met with a filtration velocity of 300 m/day and the iron scrap's height being over 60 cm. Also, it was confirmed that with fixed conditions, backwash efficiency can be recovered along with the iron scraps-utilizing T-P removal process.

In this study, the removal of T-P using iron scrap was considered to be most affected by the area of small reactor column. It is advantageous to apply this filtration system to the small scale filtration system outside the city. Especially, it can be operated at low cost by operating the T-P removal facility in the rural sewage treatment facility which is economical advantage.

4. Conclusion

The following conclusions have been made in using the iron scrap for the treatment of T-P in filtration system.

1) Reduction of the T-P concentration of the effluent to 0.2mg/L when the filtration system using iron scrap was applied to the effluent of the sewage treatment plant and lowered the color intensity suitable for the water quality standard. The optimum condition were 60 cm height and filtration rate of 300 m/day.

2) As the limited filtration duration time according to the filtration velocity of iron scrap increased from 100m/day to 500 m/day,

each bar, from 40, 32, 24, to 12, showed measurement of 4 hours.

3) As the height of filtration column of iron scrap increased to 40 cm, 60 cm and 80 cm, the efficiency of T-P removal was also increased. The removal efficiency were 68.6%, 72.9% and 74.3%, respectively. The iron scraps increased 40 cm, 60 cm, 80 cm, the efficiency of T-P removal also increased 68.6, 72.9, and 74.3%, respectively. In order to elute the T-P under 0.2mg/L, the waste iron scraps needed to be above 60 cm.

4) As the backwashing test, the removal efficiency was not recovered at 4 minutes and 7 minutes when air used only. Therefore, 60L of air and 10L of water combined were required for the best backwashing result.

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