Performance of Slag Ceramics for the Treatment of Micro-Aerobic Effluent in Contact Oxidation Reactor

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ABSTRACT

Slag ceramics, which were made from steel slag as well as a small percentage of clay and pore forming materials, were applied to a biological contact oxidation reactor for the treatment of micro-aerobic effluent. The experiment results showed that slag ceramics exhibited some favourable characteristics for removing pollution, such as lighter mass, larger specific surface area and easier biofilm-attachment compared with steel slag. In addition, a contact oxidation process filled with slag ceramics was multifunctional in pollutant removal, namely, COD, nitrogen and phosphorus were simultaneously removed. Under the hydraulic retention time (HRT) of 2.5 h, the removal efficiencies of NH$_3$-N, TN, COD and TP were 99%, 84%, 63% and 82%, respectively, and the effluent concentrations ranged in 12~27 mg/L, 0.1~1.0 mg/L, 0~0.6 mg/L and 1.0~6.8 mg/L, respectively. Mineralogical and chemical investigations revealed that the mechanisms for P removal by slag-ceramics filler, were the combination of adsorption and Ca phosphate precipitation. Therefore, the mechanisms of pollutant removal through the contact oxidation reactor filled with slag ceramics were complicated, including adsorption, precipitation, bio-oxidation and bio-reduction, etc. Meanwhile, phosphate saturation should be considered for the long-term operation.

INTRODUCTION

Phosphorus is generally the limiting nutrient for water eutrophication. Nowadays, stricter legislation on phosphorus rejection has been enacted for municipal wastewater treatment plants worldwide, because wastewater drainages are the major sources of phosphorus discharge into natural water. Among all the methods for phosphorus removal, steel slag filter is one of the most efficient and economical processes for pollutant and waste control (Dominique et al. 2013).

Steel slag is a by-product of steel industry. The annual production amount of steel slag globally ranged from 150 Mt to 230 Mt in 2012 (U. S. Geological Survey 2013), most of which was used in ways of low additional value (for instance, cement production, road construction, etc.) or disposed in specialized landfill sites. This generated an interesting potential market for economical utilization, especially for wastewater treatment.

The ability of steel slag to remove both nutrient and metal impurities from wastewater has been previously proven (Bowden et al. 2009, Pratt et al. 2007a, Korkusuz et al. 2007, Shiltona et al. 2006), and the steel slag was found as an efficient substrate for phosphorus removal in wastewater treatment. The mechanism for phosphorus removal by steel slag was interpreted, namely, precipitation with metal ions released and adsorption onto metal oxides/oxyhydroxides on the surface of steel slag (Barca et al. 2012, 2013, Pratt et al. 2007b, Shiltona et al. 2006, Vohla et al. 2011). In general, Fe, Al ions or Ca, Mg ions were inferred to represent these metals. Cristian (Barca et al. 2012) conducted a study to examine phosphorus removal by Electric arc furnace (EAF) steel slag and basic oxygen furnace (BOF) steel slag from the effluent in a constructed wetland. Based on pH data and chemical extraction, it is concluded that Ca phosphate precipitation derived from CaO-slag dissolution was the main phosphorus removal mechanism. Pratt (Pratt et al. 2007b) interpreted the mechanism of phosphorus removal by steel slag as complex actions including, surface adsorption, chemical precipitation and organic sequestration, and the adsorption of phosphorus by metal oxides/oxyhydroxides in the porous slag matrix was significant.

Previous studies demonstrated that phosphorus removal efficiencies depended on not only operating conditions, but also the characteristics of slag including, surface area and the distribution of metal ions/oxydes/oxyhydroxides, which were related to adsorption potential. As far as filter media was concerned, the slag size should be large enough
to prevent filter clogging, generally 10-40 mm particles were engaged (Shiltona et al. 2006, Barca et al. 2012). However, surface area and the adsorption potential of filter was limited. As for smaller slag particle, combined with other media as mixed media might be a choice to alleviate clogging (Korkusuz et al. 2007, Xiong et al. 2011), but compaction was still a problem. Therefore, further experiments were needed to get more porosity and a suitable size for slag filler to obtain better adsorption effect.

In this experiment, porous steel slag ceramics were prepared for biological contact oxidation of low concentration wastewater. The aim of this study was to investigate the effectiveness of slag ceramics for simultaneous pollutant removal (including organic, nitrogen and phosphorus). In addition, the study employed a combination of composition analysis, mineralogical analysis by X-ray diffraction (XRD), scanning microscopy observations and batch tests to elucidate pollutant removal processes by slag ceramisite.

**MATERIALS AND METHODS**

**Preparation of slag ceramics:** The slag ceramics were prepared from BOF-slag, clay and pore former, with a mass ratio of 5:2:1. BOF-slag and clay were collected from Tangshan Iron and Steel Co., Ltd., Hebei Province of China (as shown in Table 1), and starch was selected as pore former. Dry materials through 100 mesh sieve were first mixed in proportion in a muller, and then made into granules of 3-5 mm with water injected (35% of dry materials weight) on a disc-type pelletize. After natural drying, the granules were sintering at 1000°C for 0.5 h in a rotary kiln.

**Wastewater treatment:** As shown in Fig. 1, the contact oxidation reactor was cylindrical with an effective volume 15 L (I.D.: 0.14 m, height: 1.1 m). The media used was slag ceramics of 4-5 mesh sieve, which was packed in 0.5 m thick and supported by 0.15 m gravel. Air distribution was at 20 cm below the supporting layer through perforated pipe, which helped to maintain DO level 2~4 mg/L.

The influent was collected from the effluent of a micro-aerobic reactor for domestic wastewater treatment. The micro-aerobic reactor had stably run for about half year, which exhibited excellent ability of organic and nitrogen removal. Although the characteristics of raw wastewater varied significantly, the pretreated wastewater had rather consistent characteristics (Table 2).

During the first month of operation, HRT was set at 4 h, and the treatment efficiency of COD, TN and TP were investigated. Initially, the contact oxidation reactor was observed to have a good TP removal over 90%, but poor removal of COD and TN. It took about one month that slight biofilm developed on the filler, and the removal rates of COD and TN reached 60% and 80% respectively, which meant a successful start-up. After that, HRT was set at 2.5 h for stable running until phosphorus removal disappeared (meaning the saturation of slag ceramics for phosphorus).

In order to investigate the growth of biofilm on steel slag, batch culture was carried out in a shaking table (120 r/min) in the same time of contact oxidation reactor operation. The culture apparatus were 250 mL triangle bottles with 50 g steel slag in 100 mL wastewater. The influent of batch culture was the same as the contact oxidation reactor, and the influent exchange period was 12 h.

Both continuous-flow experiment and batch culture were carried out at room temperature in summer.

**Nitrogen removal activity of biofilm:** On the 20th day of steady running, filler samples were collected from the middle part of the contact oxidation reactor to test bio-activity of both nitrification and denitrification. Meanwhile, steel slag samples of the batch culture were also tested for comparison. Synthetic wastewater containing ammonium or nitrate (and other necessary component, such as alkalinity in nitrification and carbon resource in denitrification) was prepared as the influent of activity test. The test was accomplished in a 30°C and 120 r/min shaker, with culture time

![Fig. 1: Experiment schematic of wastewater treatment.](image)

<table>
<thead>
<tr>
<th>Materials</th>
<th>CaO</th>
<th>Fe₂O₃</th>
<th>SiO₂</th>
<th>MgO</th>
<th>MnO</th>
<th>Al₂O₃</th>
<th>P₂O₅</th>
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<tr>
<td>Steel slag</td>
<td>41.97</td>
<td>28.28</td>
<td>10.35</td>
<td>10.14</td>
<td>3.59</td>
<td>1.70</td>
<td>1.04</td>
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<tr>
<td>Clay</td>
<td>0.75</td>
<td>1.64</td>
<td>62.89</td>
<td>1.06</td>
<td>0.02</td>
<td>27.49</td>
<td>0.09</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>pH</th>
<th>COD (mg·L⁻¹)</th>
<th>NH₃-N (mg·L⁻¹)</th>
<th>TN (mg·L⁻¹)</th>
<th>TP (mg·L⁻¹)</th>
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<tbody>
<tr>
<td>20–25</td>
<td>7.2–8.0</td>
<td>20–86</td>
<td>8.2–31.4</td>
<td>9.9–33.2</td>
<td>0.8–6.0</td>
</tr>
</tbody>
</table>

Table 1: Mass fraction of steel slag and clay (W %).

Table 2: Characteristics of effluent from micro-aerobic reactor.
The samples were coated with conductive platinum before the observation of particle samples was conducted with Hitachi S-4800. SEM observations (Hitachi E-1010). EDS was performed using X-ray Energy Spectrometry (Thermo Fisher Noran7). XRD was determined by D/MaX2500PC, at 40 kV and 100 mA, Cu/ka. Elemental composition was analysed by X-ray Fluorescence Spectroscopy (XRF, ZSX Primus II).

In the experiment, chemical oxygen demand (COD), ammonia nitrogen (NH3-N), total nitrogen (TN) and total phosphorus (TP) were analysed for the influent and effluent of biological contact oxidation reactor to evaluate the removal efficiency (Chinese NEPA 2002). Meanwhile, pH and DO were simultaneously measured for the contact oxidation reactor during the experimental period.

RESULTS

Characteristics of slag ceramics before and after biofilm attachment: Fig. 2(a) showed a rough and vesicular surface of fresh slag ceramics, which was suitable for microorganisms. As shown in Fig. 2(b), slight biofilm developed on the particles after a period of cultivation. And an abundant microbial community was observed with bacillus, coccus, and a few individuals of microzoon including vorticella and rotifera.

In comparison to the steel slag, slag ceramics had a smaller apparent density and larger surface area (Table 3). Meanwhile, the surface area of slag ceramics after biofilm attachment became 2.8 times that of the fresh one. It seemed that certain components dissolved from the particle into the bulk solution during the operation, which made the material much more lacunaris. Additionally, the occurrence of simultaneous nitrification and denitrification in the biofilm indicated that the porous matrix could provide a favourable environment for both aerobic nitrifier and anaerobic denitrifier.

Mineralogical and chemical investigations of slag ceramics: As shown in Fig. 3, XRD test revealed that the fresh slag ceramics contain crystalline oxides and calc-silicates such as SiO2, MgFe2O4, Ca3Al2Si2O8, and Ca2(PO4)2. In contrast, minerals of Ca3(PO4)2 and Ca3Al2SiO8 disappeared in the spent slag ceramics, whereas Ca4K3(PO4)2 emerged.

XRF result showed that lower proportion of Ca and higher fractions of Fe and P were found in the spent particle relative to the fresh one (Table 4). The CaO level decreased 6.4% and the P level increased 1.2% in the exhausted ceramics compared to the fresh one. Pratt interpreted the phenomenon as the result of Ca dissolution and P precipitation (Pratt et al. 2007b).

The results of the semi-quantitative EDS scan taken on the surface of a representative particle from both, the fresh and spent slag ceramics (Table 5), showed a visible decrease...
in the relative concentrations of Al, Si, and Ca, but an increase of P instead. This confirmed the loss or accumulation of corresponding composition on the particle surface, as previously suggested from XRD and XRF analysis. Meanwhile, SEM-EDS analysis showed that the amorphous regions on fresh slag ceramics were predominantly composed of O, Ca, Fe, Si and Al. This confirmed the presence of metal oxides/oxyhydroxides in the slag ceramics.

Performance of pollutant removal for the contact oxidation reactor: The slag ceramics-contact oxidation reactor exhibited good effect of pollutant removal from micro-aerobic effluent (Fig. 4). During stable operation (1~45 d), the removal efficiencies of NH$_3$-N, TN, COD and TP were 99%, 84%, 63% and 82%, respectively. Meanwhile, effluent concentration ranged in 0~0.6 mg/L, 1.0~6.8 mg/L, 12~27 mg/L and 0.1~1.0 mg/L. In contrast to the intensive removal efficiencies for COD and nitrogen, phosphorus removal disappeared by the end of experiment, suggested the saturation of filler for phosphorus. Meanwhile, the outlet pH of the contact oxidation reactor was 7.5-8.6, which was higher than the corresponding pH of the inlet. It seemed that the close pH between outlet and inlet predicted the exhaustion of filler for phosphorus, and almost unchanged pH was seen after phosphorus removal disappeared. It should be noted that the previous investigation proposed a lack of phosphorus removal for micro-aerobic wastewater treatment (Chu et al. 2006, Liu et al. 2011), and the slag ceramics-contact oxidation process might compensate for the weakness, as well as enhance the effluent quality.

DISCUSSION AND CONCLUSION

Ca phosphate precipitation was supposed to be the main mechanism of P removal by Ca-rich materials, and typically the effluent pH was elevated from these materials (Pratt et al. 2007a, Barca et al. 2013). For the spent filler of contact oxidation reactor, the observed decrease in Ca content (as shown in XRF, XRD and EDS observations) may be related to the loss of reactive components such as Ca$_3$Al$_2$O$_6$ and amorphous CaO, which resulted in elevated pH. Moreover, the formation of P on the slag ceramics surface was also noticed, possibly due to the elevated pH, which was in the range of values that support Ca phosphate precipitation (Barca et al. 2013). Moreover, the loss of Ca from the slag ceramics aligned with the decreased surface area. Stable apatite was not found in the XRD test, it may be related to the operation conditions, such as low inlet P content, short hydraulic retention and short-term filter operation, since the development of stable phase needed a certain supersaturation or longer period (Drizo et al. 2002, Barca et al. 2013). Thus the form of less stable compounds such as CaK$_3$H(PO$_4$)$_2$ or amorphous may be the mechanism of Ca phosphate precipitation on the surface of slag ceramics.

Specially, the notably higher proportion of Fe in the exhausted materials may be sourced from the influent, and further study is needed to analyse the changes of Fe concentration to support the conjecture. Other elements, such as Mg and Mn, were observed to increase or decrease, which was likely due to the relative concentration or dilution, since
elements accumulation (e.g. P) as well as components release (e.g. Ca) were undergone at the same time.

Another possible way of P removal by slag ceramics was surface adsorption, especially the adsorption onto the porous area rich in amorphous metal oxides/oxyhydroxides, as the existence of these components was confirmed by SEM-EDS analysis (such as Al and Fe). Amorphous metal oxides/oxyhydroxides had the adsorption potential of inorganic ions, including phosphate from solution (Pratt et al. 2007a, Drizo et al. 2006, Yaghi et al. 2013). Generally, active hydroxyl was considered to form on the surface of metal oxides in water and participate in ligand-exchange reaction at the hydroxides-water interface (Zhang et al. 2006).

Generally, the strongly alkaline surface of Ca-rich steel slag was unsuitable for biofilm attachment, and there was hardly any microbial developed on steel slag even after long-term culture, as confirmed in Li’s research (Li et al. 2010) as well as this work. On the other hand, the less pore structure of steel slag resulted in the inefficient phosphorus removal, especially for low phosphorus in municipal wastewater. The P saturation value of steel slag was reported as 0.3 g/kg for 2-5 mm particles (Chazarenc et al. 2007), and 0.25 g/kg for 5-10 mm particles (Barca et al. 2012). By contrast, the more porous surface of slag ceramics was weakly alkaline to improve microbial development. Additionally, the P-retention ratio of slag ceramics was obviously superior to that of steel slag, i.e. 14.4 g of TP was removed by the reactor over the 78 days’ monitoring, reaching a P-retention ratio of 2.1 g/kg.

As far as the contact oxidation reactor is concerned, organic and nitrogen removal depended much on the biological oxidation/reduction (including nitrification and denitrification). However, phosphorus removal was the result of adsorption and reaction, e.g. direct adsorption onto the amorphous oxides oxyhydroxides and adsorption onto the porous matrix after chemical precipitation or organic sequestration. Although P retention capacity was promoted, exhaustion was still observed, which indicated that phosphorus adsorption was the limiting factor for the application. As the saturation time was significantly related to the influent load and filler content, this process could be favourable for the treatment of phosphorus wastewater with low strength (for example, secondary effluent of WWTP). In this respect, further research about the maximum adsorption capacity and the life expectancy of system should be considered. For the slag ceramics saturated with P, recycling in agriculture as phosphate fertilizer and amendments for acid soil may be favourable, just like P-saturated slag.

Fig. 4: Pollutants removal by slag ceramics-contact oxidation reactor.
This study showed that prilling and sintering steel slag into slag ceramics optimized the media properties to promote both biofilm growth and adsorption to remove multi pollutants. Aerobic bioreactor filled with slag ceramics performed favourably for micro-aerobic effluent treatment, which helped to keep good effluent quality. Organic and nitrogen removal in slag-ceramics reactor depended on biological oxidation/reduction. However, Ca phosphate precipitation and adsorption of metal oxides played significant role in phosphorus removal. And phosphate saturation of slag ceramics as filler should be considered for the long-term operation.

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