Oxidation of Dyeing Sludge in Supercritical Water

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Abstract. In this study, the effect of SCWO treatment, transformation characteristics of heavy metals and corrosion of Ni-based alloy 625 during dyeing sludge supercritical water oxidation (SCWO) were investigated. The experiment carried out at 580°C, 25MPa, oxidation coefficient of 1.3, reaction residence time 10min. The removal rate of COD reached 99.3% at the optimum reaction conditions which means the COD is almost completely destructed. Results of heavy metals determination showed that the concentration of Cu in the liquid products was 0.266mg/L, while Zn and Pb could not be detected under the experimental conditions. This implied that Cu, Zn and Pb in residues after SCWO treatment were more stable than that in raw sludge. The corrosion behaviour of Ni-based alloy 625 was discussed in different conditions. Consequently, it is believed that SCWO treatment is an effective alternative for safety disposal of dyeing sludge.

1. Introduction

Sludge from the textile dyeing industries contains considerable precipitated dyes, inert solids, polymer solids, metal salts and other chemicals. These pollutants in dyeing sludge may cause serious environmental problems and would be harmful to human health [1-2]. The conventional sludge treatment technologies such as incineration, landfill and composting all had inevitable problems such as pre-drying procedure, secondary pollution, high land area requirement and so on [3]. Therefore, it is significant to find an effective, economical and clean treatment technology for dyeing sludge destruction.

Supercritical water oxidation (SCWO) is an advanced technology for treatment of organic wastes with green and high effective removal [4-5]. Super critical water (SCW, Tc=647K, Pc=22.1MPa) has several distinctive properties which are very differently from the water under normal conditions. SCW with low density, low dielectric constant, and low ionization constant can provide a homogeneous reaction environment for organics, oxygen and carbon dioxide, thereby obviating interphase transfer and leading to fast reaction rates [6-7]. Organic matters can be rapidly, thoroughly decomposed into small molecular compounds such as CO₂, N₂, and H₂O less than 1min, and heteroatoms are converted to corresponding acids or salts. Previous work showed that dyeing sludge is amenable to SCWO treatment [8-10]. To the best of our knowledge, about dyeing sludge, the migration of heavy metals and the corrosion behaviour of Ni-based alloy 625 have not reported in prior work. This study aimed to investigate these characteristics during SCWO for treatment of dyeing sludge. The results and
mechanism analysis would provide theoretical foundation and guideline for the commercialization application of SCWO technology in dyeing sludge disposal.

2. Experimental

2.1. Apparatus and Materials
The experimental setup employed in this work was the same one described in our previous study [11].

The dyeing sludge was obtained from a textile wastewater treatment plant in Jiangsu province of China. Table1 shows the properties of tested sludge. The chemical reagents were analytically pure grade obtained from Tianjin Fuchen Chemical Agent Co.

| COD (mg/L) | Viscosity (mPa·s) | pH  | TN (mg/L) | Cl⁻ (mg/L) | Moisture content (wt%) | Colour |
|------------|-------------------|-----|-----------|------------|------------------------|--------|
| 99184      | >100000           | 7.5 | 3737.2    | 515.2      | 84                     | Black  |

2.2. Analysis methods
The chemical oxygen demand (COD) was analyzed by potassium dichromate method HJ 828-2017; the total nitrogen (TN) concentration was detected by alkaline potassium persulfate digestion UV spectrophotometric method HJ 636-2012; the chloride ion content was determined by silver nitrate titration GB 11896-89. The standard method of solid waste-Extraction procedure for leaching toxicity (HJ/T299-2007) was used to determine the leachability of heavy metals in the solid residues. Atomic absorption spectrophotometry was adopted to determine the contents of heavy metal.

The removal rate of COD \( X_{\text{COD}} \) is defined as follows:

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X_{\text{COD}}(\%) = \frac{[\text{COD}]_0 - [\text{COD}]_r}{[\text{COD}]_0} \times 100,
\]

where \([\text{COD}]_0\) is the initial COD concentration of the sludge with a moisture content of 88 wt% and \([\text{COD}]_r\) is the residual COD concentration of liquid products after SCWO process.

3. Results and discussion
In this paper, we found that the viscosity of moisture content of 88wt% dyeing sludge was 7050mPa·s and decreased to 6150mPa·s with adding sodium hydroxide (pH=10.5). We used moisture content of 88wt% dyeing sludge as the feedstock in all experiments for its properties suitable for transport by pipeline pump.

3.1. SCWO treatment effect
The experiments of SCWO for dyeing sludge were conducted at variable reaction temperatures (520°C, 540°C, 580°C, 600°C), oxidation coefficient (1.1, 1.2, 1.3, 1.5) and residence time (5min, 6min, 8min, 10min). The optimum reaction conditions of dyeing sludge are as follows: at 580°C, 10min with a oxidation coefficient of 1.3. The treated water quality parameters under the optimum reaction conditions are showed in Table 2.
Table 2. The treated water quality parameters under the optimum reaction conditions.

| Component     | COD (mg/L) | BOD5 (mg/L) | B/C | pH   | TN (mg/L) | Cl\textsuperscript{-} (mg/L) | Colour          |
|---------------|------------|-------------|-----|------|-----------|-----------------|-----------------|
| Feedstock     | 74387.8    | /           | /   | 10.5 | 2802.9    | 302.4           | Black           |
| Liquid product| 517.24     | 320         | 0.43| 8    | 1583.5    | 340.2           | Colourless transparent |

As shown in Table 2, the $X_{\text{COD}}$ reached 99.3% at the optimum reaction conditions which means the COD is almost completely destructed. But the concentration of TN was still 1583.5mg/L accompanied with a lower removal rate. It may due to the stable property of the nitrogenous compounds and the transformation of the nitrogen material to ammonia nitrogen. These results indicated that TN is an inert compound in the process of SCWO at moderate temperature and the liquid effluents need further treatment. The liquid product possessed sufficient biodegradability with B/C value of 0.43. The Cl\textsuperscript{-} concentration was slightly higher in treated water than in the original sludge because of the releasing of chlorine in organic chlorides through SCWO reaction. The pH of colorless transparent liquid effluents was 8. To sum up, after the removal of TN by physicochemical method, the parameters of liquid product are very suitable for biochemical process as follow-up treatment.

3.2. Transformation of heavy metals

Three typical heavy metals in dyeing sludge were tested. The content of heavy metals in raw sludge, liquid product and leach liquor of solid residues are displayed in Table 3. Among all metals analyzed, Cu, Pb and Zn were quite high and could not be ignored in the process of disposal in raw sludge. For feedstock, three heavy metals were significantly reduced after supercritical water oxidation. It is worth mentioning that, Pb and Zn have been removed completely as they are not detected in liquid products after reaction and the content of Cu was 0.266 mg/L. The Cu tended to combine with organic matters and dissolve into water again during the cooling process, hence the content of Cu was higher than other two metals [12]. The contents of heavy metals in liquid product were far below the permitted limits of Chinese EPA [13]. It has been reported that none of the heavy metals were detected in the gas phase under the SCWO conditions [14]. Heavy metals could be co-precipitated with Fe–Mn oxides which could be formed under SCWO condition or be oxidized to oxides. And Fe–Mn oxides were thermodynamically stable under oxidation environment [15]. This implied that heavy metals transferred into solid phase after SCWO and would be easily treated for final disposal.

Table 3. The content of heavy metals in raw sludge, liquid product and leach liquor of solid residues.

| Component  | Raw sludge (mg/kg, dry basis) | Feedstock\textsuperscript{*} (mg/L) | Liquid product (mg/L) | Permitted Limit\textsuperscript{[13]} (mg/L) | Leach liquor of solid residues (mg/L) | Permitted Limit\textsuperscript{[16]} (mg/L) |
|------------|-------------------------------|-------------------------------------|-----------------------|---------------------------------------------|----------------------------------------|---------------------------------------------|
| Cu         | 476.36                        | 35.43                               | 0.266                 | 0.5                                         | 10.4                                   | 100                                        |
| Pb         | 41.72                         | 3.10                                | ND                    | 0.1                                         | 1.6                                    | 5                                          |
| Zn         | 2379.86                       | 177.02                              | ND                    | 1.0                                         | 9.85                                   | 100                                        |

\textsuperscript{*}: This value is calculated using the total content of heavy metals in raw sludge.
ND: not detected

Temperature=580°C, oxidation coefficient=1.3, residence time=10min
For solid residues, the leaching toxicity of heavy metal is illustrated in Table 3. This solid product if not properly treated may cause secondary pollution to the environment. The leached amount of Cu, Pb, and Zn, which were 10.4mg/L, 1.6mg/L and 9.85mg/L respectively, greatly below the permitted limits of Chinese EPA standard [16]. It has been reported that heavy metals locked with silica matrix could be hardly leached out under natural environment [17]. Therefore, the SCWO treatment could remain heavy metals in stable tailings which greatly reduce the leachability of heavy metals.

3.3. The corrosion of Ni-based alloy 625

The corrosion of equipment materials was one of the most prominent issues that need be paid special attention in SCWO [18]. Ni-based alloy 625 is widely applied to the high temperature-high pressure region in SCWO system. In this study, the Cl⁻ concentration in the feedstock was 302.4mg/L and in liquid product was 340.2mg/L. Therefore, we further investigated the corrosion behavior of Ni-based alloy 625 samples after exposure to dyeing sludge in SCW for 60h at different conditions. The experiments carried out at oxidation coefficient of 1.3 simulated preheating (Temperature=500°C) and reaction (Temperature=580°C) stages.

Figure 1(a) displays the surface morphologies of alloy 625 samples after exposure to dyeing sludge at 500°C, 25MPa with oxidant addition for 60h simulated the conditions near the entrance of the reactor which the concentration of oxidant was the highest in all system. Ni-based alloys are known to form filiform, acicular oxides in oxidizing SCW [19]. As observed in Figure 1(a), there were mainly composed of laminar, grain and fiber structures on the surface of specimen. The EDS analysis of alloy 625 corrosion surface suggests that the relative contents of main elements follow the order of O>Cr>Ni>Fe>Mo, revealing that the surface corrosion products mainly came from the matrix of alloy 625. In Figure 1(b), the specimen was covered with numerous acicular oxides and exhibited some signs of general corrosion after exposure in oxidizing SCW of dyeing sludge for 60h at 580°C. The solubility of the inorganic salt ions decreased rapidly due to the ionic product constant of water dramatically reduced at 580°C which leads to the corrosion was dominated by high temperature oxidation. In our previous work, these acicular-like oxides are mainly composed of nickel and oxygen [19]. The EDS analysis suggests that the relative contents of main elements follow the order of Ni>O>Cr>Mo>Fe. The relative content of Ni on specimen surface at 580°C was higher than it was at 500°C mainly because of the dissolution and precipitation of Ni and formation of NiO. While the oxygen diffused inward and reacted with the inner Cr in higher temperature [20]. The experiment results suggest that the corrosion rates of alloy 625 at 500 and 580°C respectively were 0.15mm/a and 0.20mm/a, which means the Ni-based alloy 625 has excellent corrosion resistance in the oxidizing SCW of dyeing sludge.

Figure 1. SEM diagrams of Ni-based alloy 625 sample surface after exposure to dyeing sludge in SCW for 60h at 25MPa: (a)500°C,(b)580°C with oxidant(n=1.3).
4. Conclusion

The product properties of dyeing sludge for SCWO, the effect of treatment for organic compounds in dyeing sludge, the transformation characteristics of heavy metals and the corrosion of the Ni-based alloy 625 were studied in order to offer an effective evidence for dyeing sludge large-scale treatment. After SCWO of dyeing sludge at 580°C, the $X_{\text{COD}}$ reached 99.3% which confirmed that organic matter in sludge was almost completely destructed. The liquid products need a further physicochemical method for removal of TN before biochemical process as follow-up treatment. The SCWO treatment could remain Cu, Zn and Pb in stable tailings which greatly reduce the leachability of heavy metals. The Ni-based alloy 625 has excellent corrosion resistance in the oxidizing SCW of dyeing sludge.

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