Reductive transformation of p-nitrotoluene by a new iron-fly ash packing

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ABSTRACT

A new iron-fly ash packing was studied for reductive transformation of p-nitrotoluene. The packing was made of iron, fly ash and kaolin with the mass ratio of 36:7:2. A reactor was designed to investigate the long-term performance of the packing. The results showed that the reduction of p-nitrotoluene increased with decreasing pH, because the reduction potential of reaction increased with the concentration of H+. The pH was one of the key factors impacting the reductive transformation of p-nitrotoluene. Comparing iron-activated carbon packing with the new iron-fly ash packing, the reduction efficiencies were respectively 76.61% and 75.36% after 20 days. The reduction efficiency for both was around 50% at 40 days. It was evident that these two kinds of packing had no significant difference in their capability for p-nitrotoluene reductive transformation. Compared with iron-activated carbon, the new iron-fly ash packing had obvious advantages in terms of manufacturing costs and environmental pollution degradation. This study showed that the new iron-fly ash packing had good performance in reductive transformation of nitrotoluene compounds.

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Introduction

Nitrotoluene compounds are widely used in dyestuff, pesticide, rubber and pharmaceutical manufacturing (Rodgers and Bunce, 2001). They are difficult to oxidize due to the strong electron-withdrawing effect of the nitro group (Yin et al., 2012) and are recalcitrant under natural conditions. Many countries have listed nitrotoluene compounds as priority pollutants (Latifoglu and Gurol, 2003). Previous studies found that nitrotoluene compounds are highly toxic to microorganisms (Toshinari et al., 2007), amphibians (Paden et al., 2008, 2011) and mammals (Dunnick et al., 2003). The reductive transformation of nitrotoluene compounds by zero-valent iron (Bell et al., 2003) was found to be an effective way to eliminate such pollution. In addition, the resultant products could be easily used by microorganisms (Mu et al., 2004; Wu et al., 2013).

In recent years, zero-valent iron has been widely used for the treatment of different classes of pollutants such as heavy metals (Gheju, 2011; Rangsivek and Jekel, 2005), perchlorates (Ahn et al., 2014; Yu et al., 2007), azo dyes (Nam and Tratnyek, 2000; Wang et al., 2006), organic halides (Xu et al., 2006b) and nitrobenzene compounds (Mu et al., 2004; Bandstra et al., 2004). Compared with other reductants, zero-valent iron had advantages in terms of sources, price and efficiency (Noubactep, 2008). Nitrotoluene compounds were found to be transformed into toluidine compounds by zero-valent iron (Keum and Li, 2004). The overall reaction could be expressed as (Agrawal and Tratnyek, 1996):

\[
\text{ArCH}_3\text{NO}_2 + 6e + 6H^+ \rightarrow \text{ArCH}_3\text{NH}_2 + 2H_2O. \tag{1}
\]

Subsequently, zero-valent bimetals (Kim and Carraway, 2003; Xu et al., 2006a), nanoscale zero-valent iron (Crane and
Scott, 2012; Li et al., 2006) and nanoscale zero-valent bimetals (Zhu et al., 2010) were studied as reductants. These reductants increased the contact area, accelerated the transfer of electrons and improved the efficiency of the reduction. However, oxidation and agglomeration of the reductants still could not be avoided (Xu et al., 2005, 2006a, 2008).

A previous study suggested that an iron-activated carbon packing could reduce the loss and improve the utilization efficiency of iron (Li et al., 2011). The processing of activated carbon required carbonization, activation and follow-up processes (Ahmedna et al., 2000; Ioannidou and Zabaniotou, 2007), therefore the price of activated carbon was high. Fly ash is an emission product of fossil fuel combustion. Compared with activated carbon, fly ash is cheap and easy to obtain. Previous research suggested that fly ash has caused great pollution of the atmosphere, water and soil (Ahmaruzzaman, 2010). Using fly ash to replace activated carbon could decrease the manufacturing cost of the packing and cut down on the emission of fly ash.

In this study, a new iron-fly ash packing was proposed. Kaolin was used as the binder to combine fly ash and zero-valent iron in a new granular packing. The purpose of this study was to investigate the effect of pH on reductive transformation of p-nitrotoluene, examine the long-term performance of the packing, and observe the composition and morphology of the packing at different reaction times.

1. Materials and methods

1.1. Chemicals

Iron powder (200–300 mesh) and activated carbon were purchased from Tianjin Bodie Chemical Reagent Factory, China. Fly ash was taken from a boiler room. p-Nitrotoluene was purchased from Sinopharm Chemical Reagent Limited Corporation, China. Kaolin was purchased from Tianjin Damao Chemical Reagent Factory, China.

1.2. Experimental procedures

The iron powder, fly ash (activated carbon) and kaolin were mixed together with the mass ratio of 36:7:2. Then a small amount of water was added to the mixture. The above mixture was formed into 2.5-5 mm globules manually. The globules were sintered 3 hr at 600°C in a muffle furnace after being dried 20 min at 105°C in the oven. The packing was preserved in a vacuum drying oven for later use.

The schematic of the reactor system is shown in Fig. 1. The effective bed volume was 1.5 L. The hydraulic retention time (HRT) was 2 days. The flow velocity was 0.5 mL/min. All the reactions were performed under anaerobic conditions. The headspaces were replaced with nitrogen gas to drive away oxygen. The concentration of p-nitrotoluene was 1000 mg/L. The pH of the reaction was adjusted by H2SO4. In the process of reaction, samples were taken with a syringe at designated time intervals and filtered through a 0.22 μm filtration membrane before chemical analysis.

1.3. Statistical analyses and calculation

The concentration of p-nitrotoluene was analyzed by a high-performance liquid chromatograph (HPLC, Shimadzu, Japan) equipped with a UV detector on a C-18 reverse phase column (5 μm × 4.6 mm × 250 mm, Hypersil ODS2, Elite, Dalian, China). The mobile phase was a mixture of methanol and ultrapure water with volume ratio of 60:40 at a flow rate of 1 mL/min. The wavelength was set at 254 nm. The sample injection volume was 10 μL. The correlation coefficients R2 of the fitted line were above 0.999. p-Aminotoluene was analyzed by gas chromatography-mass spectrometry (GC/MS, Shimadzu, Japan). The composition and morphology of the packing was measured by scanning electron microscopy (SEM, Quanta 450, FEI, USA) with X-ray energy dispersive spectroscopy (EDS, Quanta 450, FEI, USA) and X-ray powder diffraction (XRD, Empyrean, Netherlands).

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**Fig. 1** – Schematic of the reactor system. (1) Inlet reservoir; (2) water pump; (3) valve; (4) sulfuric acid storage tank; (5) blending facility; (6) perforated plate; (7) sieve; (8) packing; (9) reactor; (10) pressure gauge; (11) outlet reservoir; (12) nitrogen tank.
2. Results and discussion

2.1. Effect of pH on reductive transformation of p-nitrotoluene

The reductive transformation of p-nitrotoluene by the new iron-fly ash packing at different pH is shown in Fig. 2.

When the pH was increased from 2 to 6, the concentration of p-nitrotoluene decreased notably. However, it decreased more slowly when the pH value was further increased from 8 to 12. At pH 2, the concentration of p-nitrotoluene was about 30 mg/L after 48 h, but higher pH values resulted in poorer performance. The results showed that the reduction of p-nitrotoluene increased with decreasing pH. The reduction potential of the reaction increased with the concentration of H+, and lower pH was beneficial for more efficient reaction.

The reduction rate constant \( k_{\text{obs}} \) for Eq. (1) was calculated using Eq. (2). \( k_{\text{obs}} \) at different pH are listed in Table 1. The results show that the reductive transformation of p-nitrotoluene is pseudo-first order (Agrawal and Tratnyek, 1996). The reduction rate constant \( k_{\text{obs}} \) decreased with increasing pH. This suggested that pH was the key factor impacting the reductive transformation of p-nitrotoluene.

The kinetics of p-nitrobenzene reduction to p-aminotoluene at pH 2 is shown in Fig. 3.

p-Aminotoluene was the reductive product of p-nitrotoluene (Agrawal and Tratnyek, 1996; Mu et al., 2004). With increasing time, the concentration of p-nitrotoluene decreased and that of p-aminotoluene increased. Due to adsorption by the packing, the total concentration of p-nitrotoluene and p-aminotoluene decreased at the early stages of the reaction. Then the packing reached adsorption equilibrium, but the total concentration of p-nitrotoluene and p-aminotoluene still decreased as a result of the volatility of p-nitrotoluene and p-aminotoluene. The loss by volatilization and adsorption was about 10%, thus chemical reduction played a main role in the reductive transformation of p-nitrotoluene.

2.2. The comparison of reductive transformation performance

The reductive transformation of p-nitrotoluene by iron-activated carbon packing and iron-fly ash packing is shown in Fig. 4. At the beginning of the reaction, 600 g of the above-mentioned reductants were added to the reactor. No additional packing was added afterwards. The pH remained at 2. The reactor was kept running for 40 days.

It can be seen in Fig. 4 that the reduction efficiencies for p-nitrotoluene were high at the beginning. The reduction efficiencies were 99.29% and 99.08% by iron-activated carbon packing and iron-fly ash packing on the first day, respectively. The reduction efficiencies were 90.14% and 90.91% after 10 days. With the extension of time, the reduction efficiencies gradually dropped. The reduction efficiencies were 76.61% and 75.36% after 20 days, respectively. The reduction efficiencies of both reactors were around 50% after 40 days. The results showed that the reduction efficiencies decreased with increasing time. Precipitates of iron oxides/hydroxides covered the surface of the packing and inhibited the contact between the packing and p-nitrotoluene, and therefore the activity of packing decreased (Li et al., 2011).

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Table 1 – Reduction rate constant \( k_{\text{obs}} \) and pH.

<table>
<thead>
<tr>
<th>pH</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
<th>10</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_{\text{obs}} ) (hr(^{-1}))</td>
<td>0.0434</td>
<td>0.0084</td>
<td>0.0046</td>
<td>0.0013</td>
<td>0.0010</td>
<td>0.0005</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.9847</td>
<td>0.9571</td>
<td>0.9176</td>
<td>0.9113</td>
<td>0.9371</td>
<td>0.9357</td>
</tr>
</tbody>
</table>

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Fig. 2 – Reductive transformation of p-nitrotoluene at different initial pH.

Fig. 3 – Kinetics of p-nitrobenzene reduction to p-aminotoluene.
The structured packing had a porous structure. Iron in the packing could break away from the granules of the packing and react with \( p \)-nitrotoluene immediately. Structured packing performs better than iron powder (Li et al., 2011). Iron powder made direct contact with the wastewater. The surface of the iron powder was covered by the oxidative products rapidly after the reaction (Agrawal and Tratnyek, 1996), and the oxidative products hampered subsequent reaction.

2.3. The composition and morphology of packing

SEM images of iron-fly ash packing before and after 40 days are displayed in Fig. 5. The results show that the surface of the packing was smooth (Fig. 5a). However, the surface of the packing became rough after 40 days of operation (Fig. 5b). There was obvious flocculent destruction and formation of corrosive pits after 40 days. The surface of the packing changed dramatically after reaction. The reductive reaction took place on the surface of the iron. As mentioned above, the activity of the packing decreased along with the changes in the packing surface. Therefore, the surface morphology of the packing played an important role in the reaction.

The EDS measurement results of the iron-fly ash packing surface before and after 40 days' reaction are displayed in Table 2. The contents of the elements Fe, C and O respectively were 37.44%, 33.13% and 20.90% before reaction. However, the contents changed notably with prolongation of reaction time. The contents of Fe, C and O were 12.86%, 37.44% and 39.74% respectively after 40 days. It was evident that Fe decreased significantly, element C increased slightly and element O increased substantially. The contents of the elements Al and Si showed little change throughout. The main reason for the decrease of Fe was that the packing was involved in the reduction of \( p \)-nitrotoluene. The main reason for the increase

Fig. 4 – Comparison of reductive transformation performance. (a) Performance of iron-activated carbon packing and (b) performance of iron-fly ash packing.

Fig. 5 – Scanning electron microscopy (SEM) images of iron-fly ash packing before (a) and after 40 days (b) reaction.
of C was that the packing adsorbed a small amount of organics, while the main reason for the increasing O was that the packing was oxidized.

The XRD analysis is displayed in Fig. 6. The corrosion product in this investigation was similar to those previously reported. It is known that the corrosion product of Fe is FeO(OH) (Huang and Zhang, 2006), which may be oxidized to magnetite Fe₃O₄ (Farrell et al., 2000) later. A previous study (Mantha et al., 2001) indicated that plugging and porosity reduction of the packing were due to the formation of corrosion products. This may be one of the important reasons why the long-term performance of the packing declined.

3. Conclusions

This study developed a novel packing, which was composed of iron powder, kaolin and fly ash. The reductive transformation of p-nitrotoluene by the new iron-fly ash packing was investigated. The results showed that the reduction of p-nitrotoluene increased with decreasing pH. The initial pH was one of the key factors in the reductive transformation of p-nitrotoluene. The long-term performance of the new iron-fly ash packing was also investigated. The reduction efficiency was still about 80% after 20 days and 50% after 40 days. Compared with iron-activated carbon packing, the reduction efficiency of the new iron-fly ash packing was also very good. The new iron-fly ash packing has advantages in terms of solid waste utilization and manufacturing cost. Making the utmost use of fly ash could reduce atmospheric, water and soil pollution. In summary, the new iron-fly ash packing showed high performance for reductive transformation of p-nitrotoluene compounds.

Acknowledgments

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References


Table 2 – Content of packing before and after reaction.

<table>
<thead>
<tr>
<th>Elemental content (wt.%)</th>
<th>Before reaction</th>
<th>10 days</th>
<th>20 days</th>
<th>40 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>37.44</td>
<td>27.24</td>
<td>17.30</td>
<td>12.86</td>
</tr>
<tr>
<td>C</td>
<td>33.13</td>
<td>35.07</td>
<td>36.57</td>
<td>37.44</td>
</tr>
<tr>
<td>O</td>
<td>20.90</td>
<td>29.06</td>
<td>38.18</td>
<td>39.74</td>
</tr>
<tr>
<td>Al</td>
<td>3.63</td>
<td>3.01</td>
<td>2.73</td>
<td>3.92</td>
</tr>
<tr>
<td>Si</td>
<td>4.43</td>
<td>4.01</td>
<td>3.86</td>
<td>3.21</td>
</tr>
</tbody>
</table>

Fig. 6 – X-ray powder diffraction (XRD) of iron-fly ash packing before and after reaction.


