Enhanced debromination of tetrabromobisphenol a by zero-valent copper-nanoparticle-modified green rusts†

Liping Fang, a Ru Liu, b Ling Xu, b Ji Li, b Li-Zhi Huang c * and Fangbai Li a c

Green rusts (GRs) interlayered with Cl−, SO42−, and CO32− were used to reduce tetrabromobisphenol A (TBBPA), which is the most widely used brominated flame retardant. The modification of GRs by copper nanoparticles (Cu NPs) greatly enhanced the reductive reactivity of GR. GR(Cl)–Cu NPs with a Cu NPs content of 0.5% had the highest reactivity toward TBBPA reduction. High pH did not favor TBBPA reduction by both GR(Cl) and GR(Cl)–Cu NPs. The presence of SO42− and CO32− inhibited TBBPA reduction by GR(Cl) and GR(Cl)–Cu NPs, whereas the inhibition effect of PO43− and humic acid was much greater than those for SO42− and CO32−. The TBBPA reduction by GR(Cl)–Cu NPs could be explained by a galvanic cell model, where electrons are transferred from GR(Cl) to Cu NPs, where TBBPA reduction occurs. Our findings demonstrate that nature-occurring Fe-bearing minerals may play an important role in the reductive transformation of TBBPA besides the biotransformation and that GR(Cl)–Cu NPs can be used for the efficient removal of reducible halogenated pollutants.

Environmental significance
As one of the most used brominated flame retardants, TBBPA is widely found in the environment. The microbial mineralization of TBBPA is usually believed to be the main reason for TBBPA removal in organic-carbon-rich environments. During the microbial mineralization process, TBBPA is first reductively debrominated to BPA under anaerobic conditions, and is then subsequently mineralized under aerobic conditions. GR is usually found in Fe(n)-containing anoxic sediment and soils. This work shows that the reductive debromination of TBBPA can also proceed at appreciable rates in abiotic systems in the presence of GRs. The modification of GR by zero-valent Cu NPs can greatly enhance the reductive debromination of TBBPA, and the engineered GR can thus be used as a potential remediation reagent for TBBPA removal.

1. Introduction
Tetrabromobisphenol A (TBBPA) is the most widely used brominated flame retardant in the world. TBBPA is a potential neurotoxicant and a thyroid endocrine disruptor, which means it poses potential risks to the ecological environment as well as to human beings. 1 As a persistent pollutant, TBBPA has been detected in soil, sediment, sludge, surface water, etc. 2 TBBPA undergoes reductive bio-debromination under anaerobic conditions, such as found in sediments and groundwater. The complete bio-debromination of TBBPA to bisphenol A (BPA) with BPA as a final debromination product has been observed under both methanogenic (within ~55 days) and sulfate-reducing (within ~112 days) conditions. 3 As a potential sink for TBBPA, anoxic sediments consist of iron-bearing minerals, which play an important role in the reductive transformation of reducible pollutants. Green rusts (GRs) are one of the most reactive iron-bearing minerals found in iron-rich anoxic sediments and soils. GRs are intermediate phases formed by the partial oxidation of Fe(n) minerals or the partial reduction of Fe(III) (hydr)oxides. 4 GRs are a type of mixed Fe(n) and Fe(III) iron minerals with a unique layered structure, 5 and have the general formula of [FeI n−xFeII x ]m (OH)3]x+ [(x/n)A n− , nH2O]− , where A n− is the intercalated anion (A n− = Cl−, SO42−, CO32−) and x is the molar fraction of Fe(III). As a strong reductant, GRs play an important role in the transformation of reducible pollutants, such as chlorinated solvents, 6,7 antimony, 8 nitrate, 9 chromium, 10 neptunyl (NpVI), 11 uranium(UVI) 12 and technetium (TcVII). 13 The reductive dehalogenation of TBBPA by GRs is rarely studied, although GRs may play an important role in the transformation of TBBPA.
Owing to their high reductive reactivity and the opportunity to inject reactive GRs into contaminant plumes, engineered synthetic GRs have been widely used as dehalogenation reductants in environmental remediation.14–16 The intercalation of surfactant anions into GR can greatly enhance the reductive dehalogenation due to the sorption of hydrophobic halogenated pollutants onto the surfactant interlayered GRs.14 The presence of amino acids, such as glycine, can reduce the formation of toxic byproducts, i.e., chloroform, during the dehalogenation of carbon tetrachloride by GRs.17 Our recent work demonstrated how the dehalogenation reactivity of GR can be turned off/on by a silicate/glycine switch, which overcome the problems of the reactivity loss during the application of GRs for soil and groundwater remediation.16 The modification of GRs by a metal is another efficient way to enhance the reductive reactivity of GRs, and the enhancement options could even be combined, showing a synergistic effect for the significantly improved reactivity of GRs.15

The introduction of a second metal, such as Cu, Ni, Pb, Pt, Ag, or Au, to iron-bearing reductants could significantly increase the reductive activity of iron-bearing reductant.18–24 A galvanic cell model has been generally accepted to explain the enhanced reactivity, where iron-bearing reductants are oxidized and transfer electrons to the generated reactive metal nanoparticles. Oxidant pollutants are reduced much faster on the surface of the generated reactive metal nanoparticles compared to iron-bearing reductants, which results in an enhancement of the reductive reactivity. The introduction of Au or Ni nanoparticles (NPs) to ZVI has been recently been reported to be an effective way to enhance the debromination of TBBPA by ZVI.22,23 Cu is one of the low-cost and abundant metals, and Cu-modified iron-bearing reductants are promising for real applications. Cu-modified ZVI bimetallic systems have shown high reductive dehalogenation reactivity.25,26 Cu-modified GR systems often use Cu2+ as a precursor for the in situ generation of zero-valent Cu nanoparticles on the GR surface,27 however, the direct modification of GRs by zero-valent Cu has never been studied. On the other hand, the formation of mono-valent Cu rather than the zero-valent form of Cu has been studied after the addition of Cu2+ into GR suspensions in our recent work.15 The formation of zero-valent Cu is important for ensuring high reductive reactivity because of the higher electron-donating property and higher electron conductivity of zero-valent Cu compared to mono-valent Cu. Furthermore, the in situ generation of active Cu species from Cu2+ reduction by GRs results in the oxidation of GRs to other iron oxides with less electron-donating capabilities, which may suppress the electron transfer from GRs to Cu.

In this work, the influences of interlayered anions, the pH, and background anions on the reductive debromination of TBBPA by GRs were investigated. Furthermore, Cu NPs were introduced to a GR reductant to enhance the reductive debromination of TBBPA by GRs. The enhanced reactivity of GR(Cl)–Cu NPs was systematically compared to GR and GR modified with Cu2+, and the mechanism for the enhanced debromination was investigated.

2. Materials and methods

2.1 Synthesis and characterization of GRs

GRs interlayered with Cl–, SO4–, and CO32– were synthesized through the air oxidation of a ferrous hydroxide [Fe(OH)2] precipitate in aqueous solution.28 The synthesis takes place in a 500 mL beaker. For the synthesis of Cl–-interlayered GR (GR(Cl)), 0.035 mol FeCl2·4H2O was dissolved in 50 mL 1 mol L–1 NaOH under magnetic stirring. Then, 150 mL deionized water was quickly added to form an Fe(OH)2 suspension. The Fe(OH)2 suspension was partially oxidized in air with magnetic stirring at 380–400 r min–1. The GR synthesis was completed when the pH was about 7.8 and the oxidation time was about 60 min. For the synthesis of SO42–-interlayered GR (GR(SO4)), 0.035 mol FeSO4·7H2O was used and the synthesis time was 90 min. CO32–-Interlayered GR (GR(CO3)) was synthesized via vigorous stirring of the as-synthesized GR(SO4) suspension in the presence of 7.42 g NaCO3 for 3 h. The as-synthesized GRs were transferred to a glovebox, washed with O2-free deionized water, and stored in the dark till further use.

2.2 Synthesis of Cu NPs

The Cu NPs were synthesized using a liquid-phase reduction method.18 Briefly, 0.05 mole CuSO4·5H2O was dissolved in 50 mL deionized water, followed by the addition of 0.7 mole glacial acetic acid under magnetic stirring. The pH of the solution was adjusted to around 10 with ammonium hydroxide. Then, 0.1 mole hydrazine hydrate was added, followed by stirring for 1 h. The Cu NPs were collected via centrifugation at 11 000 r min–1 for 15 min. The as-synthesized Cu NPs were washed with O2-free ethanol and water, and then stored in a glovebox until further use.

2.3 Synthesis of GR(Cl)–Cu NPs and GR(Cl)–Cu2+

GR interlayered with Cl– anions was used for the synthesis of GR(Cl)–Cu NPs. First, 0.035 mol FeCl2·4H2O was dissolved in 50 mL 1 mol L–1 NaOH under magnetic stirring. Then, 150 mL deionized water was quickly added to form Fe(OH)2 suspensions. The Cu NPs were sonicated for 10 min and added into the Fe(OH)2 suspensions. The mixture of Cu NPs and Fe(OH)2 suspension was partially oxidized in air with magnetic stirring at 380–400 r min–1. The synthesis was completed when the pH was about 7.8 and the oxidation time was about 60 min. For the synthesis of GR(Cl)–Cu2+, the as-synthesized GR(Cl) was amended with CuSO4 solution, followed by being well dispersed by stirring for 300 min. The as-synthesized GR(Cl)–Cu hybrid with different Cu mass loadings were designated as GR(Cl)–Cu NPs(X) or GR(Cl)–Cu2+(X), X = 0.2%, 0.5%, 1.0%, 2.0%. For the measurement of the GR and GR(Cl)–Cu NPs concentration, the as-synthesized GRs or GR(Cl)–Cu NPs suspension was magnetically stirred for 10
min in an anaerobic environment. A certain volume of GRs or GR(Cl)–Cu NPs suspension was transferred to a centrifuge tube. The supernatant was removed after centrifugation, and the remaining sludge was freeze dried for 24 h. The concentration of the suspensions was calculated by the dry mass/the volume of the suspensions.

2.4 TBBPA degradation

The debromination of TBBPA by GR(Cl), GR(SO4), and GR(CO3) was carried out in Tris buffer solution (1 mol L⁻¹, pH = 8.0). The GR dosage was 0.5 g L⁻¹ (added as a suspension), while the initial TBBPA concentration was 15 mg L⁻¹, and the reaction temperature was 25 °C. The reaction mixture was shaken on a shaking table and sampled at 10, 30, 60, 180, 360, and 960 min. The TBBPA in each sampled suspension was determined by high performance liquid chromatography (HPLC) after filtration using 0.22 μm mixed cellulose ester membrane. The removal efficiency for TBBPA by GRs or GR(Cl) was determined by eqn (1):

\[
\text{Removal efficiency} = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)
\]

The mass normalized removal efficiency of TBBPA (qₑ) was calculated by eqn (2):

\[
q_e = \frac{(C_0 - C_e)V}{m} \times 100\% \quad (2)
\]

where \(C_0\) and \(C_e\) are the initial and final concentration of TBBPA (mg L⁻¹), \(V\) is the volume of reaction mixture (L), and \(m\) is the mass of GR (g).

The effect of Cu NPs content on TBBPA reduction by GR(Cl)–Cu NPs suspension was determined by GR(Cl)–Cu NPs(X), \(X = 0.2\%, 0.5\%, 1.0\%, 2.0\%\) wt%. TBBPA reduction by GR(Cl)–Cu N₂(X) and by pure Cu NPs was conducted as a comparison. The dosage of reductants was 0.5 g L⁻¹, while the initial TBBPA concentration was 15 mg L⁻¹, and the reaction temperature was 25 °C. The reaction mixtures were shaken on a shaking table and sampled at 20, 30, 60, 120, 300, and 720 min following TBBPA determination (see below). The effect of pH on TBBPA reduction by GR(Cl) and GR(Cl)–Cu NPs was studied in Tris buffer with different initial pH values from 8.0 to 10.5. The reaction was carried out for 720 min, followed by TBBPA determination. In order to study the effect of background anions on TBBPA debromination, different background anions, including \(\text{SO}_4^{2-}\), \(\text{CO}_3^{2-}\), \(\text{PO}_4^{3-}\), and humic acid (in terms of carbon content) were added to the reaction suspensions with a final concentration of 10, 20, 30, 40, and 50 mg L⁻¹. The reaction was carried out in Tris buffer at pH 8.0. All the experiments were carried out under strictly O₂-free conditions in the glovebox (O₂ < 0.1 ppm). Thus, possible ‘OH generation from O₂ activation could be excluded.

2.5 Analytical methods

The concentration determination of Fe²⁺ and Fe³⁺ in the GRs and in the solutions were performed in the glovebox using a modified phenanthroline method.\(^{29,30}\) Cu²⁺ and Cu⁺ in the GR–Cu NPs samples were determined using the 2,9-dimethyl-1,10-phenanthrolinespectrophotometric method at 457 nm.\(^{31}\) Total Cu (Cu²⁺ + Cu⁺) was determined after the reduction of Cu²⁺ to Cu⁺ with excess hydroxylamine hydrochloride, and Cu²⁺ was calculated by subtraction. TBBPA was analyzed by an HPLC instrument (Agilent 1260) equipped with an C18 column (5 μm, 150 mm × 4.6 mm). The eluent consisted of 10 mM phosphoric acid solution (pH = 3) in acetonitrile mixture (1/3, v/v). The injection volume was 20 μL and the flow rate was 0.8 mL min⁻¹. UV-vis detection was carried out at a wavelength of 219 nm. The concentration of Br⁻ ions was determined by ion chromatography (IC, 882 Compact IC Plus, Switzerland) equipped with a Supp 5 analytical column (100 × 4 mm i.d.). The eluent consisted of 0.30 mol L⁻¹ NaHCO₃ and 0.24 mol L⁻¹ Na₂CO₃ and the flow rate was 1.4 mL min⁻¹. The extent of debromination was calculated as per eqn (3):

\[
\text{Debromination extent} = \frac{[\text{Br}^-]}{[\text{TBBPA}] \times N} \times 100\% \quad (3)
\]

where [Br⁻] is the concentration of Br anions in the reaction solution, [TBBPA] is the initial concentration of TBBPA, and \(N\) is the number of Br atoms in TBBPA (N = 4).

The debromination products of TBBPA were identified using an Agilent 1200 series liquid chromatography instrument coupled to an Agilent 6410 electrospray triple quadrupole mass spectrometer (LC-MS) with an Agilent ZORBAX Eclipse Plus C18 reversed-phase column (25 cm × 4.6 mm × 5 mm particle size; Agilent, Santa Clara, USA). The mobile phase was a mixture of methanol/water (v/v, 8/2) and the flow rate was 1 mL min⁻¹. The mass spectrometric analysis was performed using electrospray ionization (ESI) in the negative ion mode with a scan range from 45 to 700 amu.

X-ray diffraction (XRD) data were collected in the angular 2θ range 5–60° using a Bruker AXS D8-Focus X-ray diffractometer (Germany). Transmission electron microscopy (TEM) images were obtained using a JEOL transmission electron microscope with an accelerating voltage of 200 kV. The reductants were suspended in O₂-free water under vigorous stirring. Droplets of the suspensions were dried on a microscope carbon grid, followed by TEM observation. Scanning electron microscopy (SEM) images were observed by a Quanta 200 microscope (FEI Company, USA) operating at 10 kV.

3. Results and discussions

3.1 Characterization of GRs and GR(Cl)–Cu NPs

The XRD patterns of the as-synthesized GR(SO₄), GR(CO₃), and GR(Cl) were in agreement with the observation by others (Fig. 1a–c).\(^{28}\) The XRD patterns of GR(Cl) and GR(Cl)–Cu NPs...
were almost the same, demonstrating the GR structure was kept intact in the presence of the Cu NPs (Fig. 1d). In contrast, the XRD patterns of GR(Cl)–Cu\(^{2+}\) showed that GR(Cl) is transformed to lepidocrocite and magnetite upon the addition of Cu\(^{2+}\) (Fig. S1†). The XRD patterns of Cu NPs showed diffraction peaks at 2\(\theta\) values of 43.6° and 50.8°, corresponding to the (111) and (200) planes of fcc structure of Cu (Fig. 1e).\(^{32}\) No diffractions from Cu NPs were observed in the XRD patterns of GR(Cl)–Cu NPs, which may be attributed to the low concentration of Cu NPs in the GR(Cl)–Cu NPs. The as-synthesized GR(Cl) particles had a hexagonal morphology with a lateral dimension of 100–400 nm, as shown by TEM (Fig. 2a). Cu NPs with a particle size of 20–100 nm were located on the basal plane of GR(Cl) (Fig. 2b). High-resolution TEM showed the (111) plane of Cu, which resulted in diffraction peaks at 43.6° in the XRD pattern.

### 3.2 TBBPA reduction by GR(Cl), GR(SO\(_4\)), and GR(CO\(_3\))

The three types of GRs all showed debromination activity toward TBBPA, indicating GRs may play a role in the transformation and fate of TBBPA in the environment. The debromination of TBBPA by GR(Cl), GR(SO\(_4\)), and GR(CO\(_3\)) all ceased after 720 min. The reactivity of the GRs toward TBBPA reduction depended on the intercalated anions, with Cl\(^-\) intercalated GR showing a higher reactivity than GRs intercalated with SO\(_4^{2-}\) and CO\(_3^{2-}\) (Fig. 3a). The removed amount of TBBPA by GR(Cl) was 21.44 mg g\(^{-1}\) with a removal efficiency of 71.47%, which was three times that by GR(SO\(_4\)) and around seven times that by GR(CO\(_3\)). The structural Fe\(^{II}\) in GR with a high electron-donating capability was responsible for the reductive activity of the GRs. Thus GR(Cl) with a higher Fe\(^{II}\) content could reduce TBBPA faster than GR(SO\(_4\)) and GR(CO\(_3\)).\(^{33}\) Despite having the highest reductive strength, GR(Cl) was also less stable and easier to undergo dissolution in the natural environment compared to GR(SO\(_4\)) and GR(CO\(_3\)).\(^{16}\) On the other hand, GR(CO\(_3\)) was more stable than GR(SO\(_4\)) and GR(Cl), but had the lowest activity toward TBBPA reduction. Thus, the transformation of TBBPA by the different types of GRs in the natural environment could be complex.

### 3.3 Effects of Cu NPs content on TBBPA reduction by GR(Cl)–Cu NPs

The presence of Cu NPs can enhance the reductive activity of GR(Cl) toward TBBPA debromination. The reactivity of GR(Cl)–Cu NPs increased with the Cu NPs content increasing from 0 to 0.5 wt% (Fig. 3b). GR(Cl)–Cu NPs(0.5%) showed the highest TBBPA removal efficiency of 92.11%. Further increasing the Cu NPs content in GR(Cl)–Cu NPs from 0.5 to 2 wt% resulted in a decrease in the reactivity of GR(Cl)–Cu NPs toward TBBPA debromination (Fig. 3b), and the TBBPA removal efficiency dropped from 92.11% to 77.03%. In contrast, pure
Cu NPs showed negligible reductive reactivity toward TBBPA debromination. These phenomena can be explained by a galvanic cell model, in which electrons are transferred from GR(Cl) to the Cu NPs, where TBBPA reduction occurs. Cu NPs are stronger reductants than GR, which result in a faster debromination of TBBPA on Cu NPs than on GR. However, the limited reductive reactivity of pure Cu NPs suggests the possible fast deactivation of the Cu NPs surface due to corrosion in water. In the GR(Cl)–Cu NPs system, a galvanic cell may form where the GR(Cl) dissolves and act as a “sacrificial anode” to avoid corrosion of the Cu NPs. Too high a Cu NPs content in GR(Cl)–Cu NPs leads to an imbalanced proportion of electron donaters (GR(Cl)) and electron acceptors (Cu NPs), which may result in a decrease in the overall reductive activity of the system.

The experimental kinetics were fitted to the pseudo-first-order and pseudo-second-order kinetics by a linear and a non-linear method (Tables 1 and 2). The experimental TBBPA removal amount was very close to the theoretical values obtained by the pseudo-second-order non-linear method. This suggested that the TBBPA debromination by GR(Cl)–Cu NPs followed the pseudo-second-order kinetic model.

3.4 Effects of pH
The reactivity of both GR(Cl) and GR(Cl)–Cu NPs toward TBBPA reduction declined with the pH going from 8 to 10.5 (Fig. 4a, S2 and S3†). When the reaction pH increased from 8.0 to 10.0, the TBBPA removal efficiency by GR(Cl) decreased from 60.24% to 20.29% and that by GR(Cl)–Cu NPs(0.5%) decreased from 78.12% to 34.06%. Under alkaline conditions, GRs may be transformed to other types of iron oxides with lower reductive reactivity, and the electron-donating capability of the transformed GRs to Cu NPs may also be suppressed.34 This will eventually lead to a lower dissolution of GR during the reaction. We thus determined the released free Fe²⁺ in the reaction solution as a consequence of the GR dissolution. The concentration of released free Fe²⁺ in both

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Table 1 Pseudo-first-order linear kinetics parameters and nonlinear kinetics parameters for TBBPA removal by GR(Cl)–Cu NPs

<table>
<thead>
<tr>
<th>Material</th>
<th>( q_{\text{exp}} ) (mg g⁻¹)</th>
<th>( k_{\text{obs}} ) (min⁻¹)</th>
<th>( q_{\text{eq}} ) (mg g⁻¹)</th>
<th>( R^2 )</th>
<th>( q_{\text{exp}} ) (mg g⁻¹)</th>
<th>( k_{\text{obs}} ) (min⁻¹)</th>
<th>( q_{\text{eq}} ) (mg g⁻¹)</th>
<th>( R^2 )</th>
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<tr>
<td>GR(Cl)</td>
<td>17.97</td>
<td>0.0032</td>
<td>16.55</td>
<td>0.6180</td>
<td>21.44</td>
<td>0.0018</td>
<td>19.29</td>
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<td>GR–CuNPs(0.2%)</td>
<td>19.89</td>
<td>0.0121</td>
<td>20.22</td>
<td>0.8363</td>
<td>22.71</td>
<td>0.0056</td>
<td>21.53</td>
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<td>GR–CuNPs(0.5%)</td>
<td>22.95</td>
<td>0.0185</td>
<td>22.27</td>
<td>0.8478</td>
<td>27.63</td>
<td>0.0084</td>
<td>25.36</td>
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<td>GR–CuNPs(1.0%)</td>
<td>20.92</td>
<td>0.0163</td>
<td>21.83</td>
<td>0.8418</td>
<td>23.98</td>
<td>0.0073</td>
<td>22.92</td>
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<td>GR–CuNPs(2.0%)</td>
<td>20.40</td>
<td>0.0148</td>
<td>21.50</td>
<td>0.8236</td>
<td>23.11</td>
<td>0.0066</td>
<td>22.20</td>
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Table 2 Pseudo-second-order linear kinetics parameters and nonlinear kinetics parameters for TBBPA removal by GR(Cl)–Cu NPs

<table>
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<tr>
<th>Material</th>
<th>( q_{\text{exp}} ) (mg g⁻¹)</th>
<th>( k_{\text{obs}} ) g mg⁻¹ min⁻¹</th>
<th>( q_{\text{eq}} ) (mg g⁻¹)</th>
<th>( R^2 )</th>
<th>( q_{\text{exp}} ) (mg g⁻¹)</th>
<th>( k_{\text{obs}} ) g mg⁻¹ min⁻¹</th>
<th>( q_{\text{eq}} ) (mg g⁻¹)</th>
<th>( R^2 )</th>
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<tr>
<td>GR(Cl)</td>
<td>21.44</td>
<td>0.1108</td>
<td>21.73</td>
<td>0.9996</td>
<td>21.44</td>
<td>0.0141</td>
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<td>GR–CuNPs(0.2%)</td>
<td>22.71</td>
<td>0.1209</td>
<td>22.98</td>
<td>1.0000</td>
<td>22.71</td>
<td>0.0054</td>
<td>22.91</td>
<td>0.9986</td>
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<tr>
<td>GR–CuNPs(0.5%)</td>
<td>27.63</td>
<td>0.0850</td>
<td>28.00</td>
<td>0.9998</td>
<td>27.63</td>
<td>0.0043</td>
<td>27.09</td>
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<tr>
<td>GR–CuNPs(1.0%)</td>
<td>23.98</td>
<td>0.1007</td>
<td>24.31</td>
<td>1.0000</td>
<td>23.98</td>
<td>0.0038</td>
<td>24.59</td>
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<td>GR–CuNPs(2.0%)</td>
<td>23.11</td>
<td>0.1163</td>
<td>23.42</td>
<td>1.0000</td>
<td>23.11</td>
<td>0.0043</td>
<td>23.72</td>
<td>0.9984</td>
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TBBPA–GR(Cl) and TBBPA–GR(Cl)–Cu NPs systems decreased with increasing pH (Fig. 4b), which suggested that a high TBBPA removal efficiency is correlated to a high GR dissolution. The higher concentration of released Fe$^{2+}$ ions in the TBBPA–GR(Cl)–Cu NPs system compared to the TBBPA–GR(Cl) system also confirmed the accelerated GR dissolution in the galvanic cell model. Furthermore, the high pH results in negatively charged TBBPA molecules, which may repel the negatively charged GR with a point of zero charge of ~8.5. A similar phenomenon was observed for tetrachloroethene reduction by GR(Cl) in the presence of Cu(u), where alkaline conditions decreased the reactivity of GR(Cl)–Cu(u). Acidic conditions were not explored due to the possible dissolution of GR, which may have led to the release of free Fe(u) ions into the reaction solution with low reactivity.

3.5 Effect of the background anions

The presence of SO$_4^{2–}$ and CO$_3^{2–}$ inhibited TBBPA reduction by GR(Cl) and GR(Cl)–Cu NPs, whereas the inhibition effect of PO$_4^{3–}$ and humic acid were greater than that of SO$_4^{2–}$ and CO$_3^{2–}$ (Fig. 5). TBBPA (pK$_{a1}$ = 7.5, pK$_{a2}$ = 8.5) exists as an anion form at pH 8, at which pH all the experiments were carried out. The sorption of negatively charged TBBPA onto the surface of GRs may favor TBBPA reduction by GRs. Thus, the presence of anions, such as SO$_4^{2–}$, CO$_3^{2–}$, and PO$_4^{3–}$, has a negative effect on TBBPA reduction due to the competition for both the GRs and Cu reactive sites.

A very similar inhibition effect of SO$_4^{2–}$ and humic acid on TBBPA reduction was observed in both the GRs and GR–Cu NPs systems. In the presence of 50 mg L$^{-1}$ SO$_4^{2–}$, the TBBPA removal efficiency decreased by 57% for GR(Cl) and 51% for GR(Cl)–Cu NPs. This was supported by the higher Fe$^{2+}$ content in GR(Cl) and GR(Cl)–Cu NPs after reaction in the presence of SO$_4^{2–}$. A huge negative effect of HA on TBBPA reduction by GR (decrease of 93%) and GR–Cu NPs (decrease of 86%) was observed. This could be attributed to the strong HA adsorption onto the GR surface through complex formation, such as complexation between iron/iron oxide and the various types of functional groups in HA (e.g., carboxylate, phenolic, and carbonyl groups). The oxidation of GR by HA may also inhibited TBBPA reduction by the GRs (see below).

For CO$_3^{2–}$ and PO$_4^{3–}$, the inhibition effect was greater in GR compared to in the GR–Cu NPs systems due to the altered reductive sites from GR to Cu NPs. In the presence of 50 mg L$^{-1}$ CO$_3^{2–}$/PO$_4^{3–}$, the TBBPA removal efficiency decreased by 69%/81% for GR(Cl) and 38%/48% for GR(Cl)–Cu NPs. For the GR system, CO$_3^{2–}$ could react with Fe$^{2+}$ and precipitate as FeCO$_3$ (siderite) on the reductant’s surface, which inhibited TBBPA reduction by GR. Also, the higher affinity between the positively charged Fe hydroxide layer in GR and the CO$_3^{2–}$ anions compared to Cl$^{–}$ anions may lead to the formation of GR(CO$_3$)$_2$ via ion exchange. The lower reactivity of GR(CO$_3$)$_2$ toward TBBPA reduction compared to GR(Cl) led to the decreased reactivity of GR(Cl) in the presence of CO$_3^{2–}$. In addition, the corrosion/dissolution of GR during the reaction resulted in the release of ferrous ion from the surface of GRs. In the presence of PO$_4^{3–}$, ferrous ions easily precipitate as Fe$_3$(PO$_4$)$_2$ on the surface of GRs and greatly inhibit TBBPA reduction. The slightly stronger inhibition effect by PO$_4^{3–}$ observed in the GR system compared to in the GR–Cu NPs system could be attributed to the fact that Fe$_3$(PO$_4$)$_2$ precipitate formation on Cu surface may be less favored compared to on the more ferrous-rich GR surfaces. This observation is in line with our proposed galvanic cell model, where there is a shift of TBBPA reduction site from the GR to the Cu surface in the GR–Cu NPs system. For the GR–Cu NPs system, the inhibition effect only results from the competitive adsorption for Cu active sites between CO$_3^{2–}$/PO$_4^{3–}$ and TBBPA. Thus, the presence of CO$_3^{2–}$/PO$_4^{3–}$ has a greater inhibition effect in GR compared to in GR–Cu NPs systems.

The effects of anions/humic acid on the change of the content and valence of Fe and Cu in the material were investigated. In the presence of SO$_4^{2–}$, PO$_4^{3–}$, and CO$_3^{2–}$, more Fe$^{2+}$...
was left in both GR and GR–Cu NPs after reaction (Fig. 6). In contrast, the Fe²⁺ content in GR(Cl) and GR(Cl)–Cu NPs was slightly lower in the presence of HA (Fig. 6). This demonstrated that the presence of HA leads to the GR oxidation by HA. The oxidation of Fe(II) by HA has also been observed by others.⁴⁰,⁴¹ The combined effect of adsorption onto GR and the consumption of electrons in GR by HA greatly inhibited TBBPA reduction by the GRs. In the GR/Cu NPs system, Cu⁰ was transformed to Cu⁺ in the absence or presence of background anions and humic acid (Fig. S4†). This was further confirmed by the formation of Cu₂O after GR(Cl)–Cu NPs reaction with TBBPA (Fig. S5†). The presence of background anions and humic acid had little influence on the Cu⁺ production. This demonstrated that the background anions and humic acid mainly influence the reaction via interaction with the GR.

### 3.6 Debromination products

The reductive debromination of TBBPA by GR(Cl) and GR(Cl)–Cu NPs resulted in the formation of tribromobisphenol A (tri-BBPA), dibromobisphenol A (di-BBPA), and monobromobisphenol A (mono-BBPA), which were identified by LC-MS. The related mass spectra are shown in Fig. S3†. Two isomers of di-BBPA were observed by LC-MS, which was
in line with a previous study. The released Br\(^{-}\) anions were identified by ion chromatography, with the extent of debromination shown in Fig. 7. The doping of Cu NPs into GR(Cl) greatly enhanced the debromination rate and increased the debromination extent from \(\sim 60\%\) to \(\sim 80\%\).

### 3.7 Mechanisms of the enhanced reduction

In order to further reveal the mechanism of the enhanced reduction of TBBPA by GR(Cl)–Cu NPs, the reactivity of the GR(Cl)–Cu NPs system was compared to that of the GR(Cl)–Cu\(^{2+}\) counterparts. The oxidation rate of Fe\(^{II}\) in GRs and the release of Fe\(^{2+}\) cations into the reaction solution were also investigated. A higher reactivity of GR(Cl)–Cu NPs toward TBBPA reduction was observed compared to their GR(Cl)–Cu\(^{2+}\) counterpart (Fig. 8). This demonstrated that the addition of Cu\(^{2+}\) into GR suspensions cannot generate the same system with a reactivity as high as the GR(Cl)–Cu NPs. This could be attributed to: i) the copper species formed, i.e., mono-valent copper is formed instead of zero-valent copper.

There was evidence of mono Cu generated in our GR(Cl)–Cu\(^{2+}\) system (Fig. S4 and S5†). Mono-valent copper has a lower electron-donating capability than zero-valent copper, which results in a lower reactivity toward TBBPA reduction. Also, the lower electron conductivity of mono-valent copper may result in a lower electron-transfer efficiency compared to zero-valent copper, whereas a fast electron transfer between GR, Cu, and TBBPA is essential for TBBPA reduction in a galvanic cell model; ii) the addition of Cu\(^{2+}\) inevitably led to the oxidation of GR with the formation of less reactive iron oxides, as shown by the XRD data (Fig. S1†). This consumes the electrons in the GR, which acts against the electron-donating process from GR to Cu and the latter reduction of TBBPA. This effect may have little impact of the reductivity since the Cu\(^{2+}\) addition was only 0.5%. However, the transformation of GR was evidenced even though the Cu\(^{2+}\) dosage was low. This may be attributed to the instability of the GR structure. The transformation of GR to the more stable iron oxide may occur once the oxidation of GR was triggered by the Cu\(^{2+}\) addition. On the other hand, we

![Fig. 7](image1)

**Fig. 7** Evolution of Br\(^{-}\) anions during TBBPA reduction by GR(Cl) (a) and GR(Cl)–Cu NPs(0.5%) (b). Experimental conditions: GR(Cl) and GR(Cl)–Cu NPs(0.5%) dosage = 0.5 g L\(^{-1}\), pH = 8, initial TBBPA concentration = 15 mg L\(^{-1}\).

![Fig. 8](image2)

**Fig. 8** Comparison of TBBPA reduction by GR(Cl), GR(Cl)–Cu NPs, and GR(Cl)–Cu\(^{2+}\) (a), and oxidation of structural Fe\(^{II}\) in GR(Cl), GR(Cl)–Cu NPs, and GR(Cl)–Cu\(^{2+}\) during TBBPA removal, respectively (b). Experimental conditions: reductants dosage = 0.5 g L\(^{-1}\), pH = 8, initial TBBPA concentration = 15 mg L\(^{-1}\).
did observe a lower reactivity in GR–Cu$^{2+}$(0.5%) compared to GR–Cu NPs(0.5%), where no oxidation of GR occurred (Fig. 8a). We thus speculate that the formation of less reactive iron oxides was the reason for the decreased reactivity. This phenomenon can also be explained by the fact that the generated mono-valent Cu in the GR/Cu$^{2+}$ system is less active than zero-valent Cu in the GR/Cu NPs system, but quantification of the contribution from each side is very difficult. Furthermore, the generated Cu active sites are most likely in direct contact with the oxidized GR, i.e., less reactive iron oxides, which is a poor electron conductor/shuttle and suppresses the electron transfer from GR to Cu.

The oxidation rate of Fe$^{II}$ in GR in the different systems followed the same order of the TBBPA reduction rate: GR(Cl)–Cu NPs > GR(Cl)–Cu$^{2+}$ > GR$_3$. This implied that the electron transfer from GR to Cu occurs because the oxidation rate of Fe$^{II}$ in GR should be the same in different systems if GR and Cu both act as discrete reductants. GR(Cl) was transformed to magnetite (Fe$_3$O$_4$) and goethite (α-FeO(OH)) after reaction with TBBPA (Fig. 9). A similar oxidation product was also observed after GR(Cl) was reacted with nitrate. TBBPA reduction occurs on Cu NPs surface. Subsequently, Cu$^{+}$ was produced as an intermediate product from Cu oxidation (Fig. 6b) and GR transformed to Fe$_3$O$_4$ and α-FeO(OH) (Fig. 9):

$$C_{15}H_{12}Br_4O_2 + 3Cu \rightarrow C_{15}H_{15}BrO_2 + 3Br^- + 3Cu^+ \quad (4)$$

$$5Cu^+ + 3Fe^{II}Fe^{III}(OH)_6Cl \rightarrow 5Cu + 4Fe_3O_4 + 3Cl^- + 8H^+ + 8H_2O \quad (5)$$

$$3Cu^+ + Fe_3Fe(Fe(OH))_6Cl \rightarrow 3Cu + 4FeO(OH) + Cl^- + 4H^+ \quad (6)$$

Thus all our evidence supported the galvanic cell mode: electrons were transferred from GR to Cu active sites, where TBBPA was reduced. The proposed enhanced reduction of TBBPA by GR(Cl)–Cu NPs is illustrated in Fig. 10.

The microbial mineralization of TBBPA is usually believed to be the main reason for TBBPA removal in organic-carbon-rich environments. During the microbial mineralization process, TBBPA is first reductively debrominated to BPA under anaerobic conditions, and is subsequently mineralized under aerobic conditions. GR is usually found in Fe$^{II}$)-containing anaerobic sediment and soils. This work showed that the reductive debromination of TBBPA can also proceed at appreciable rates in abiotic systems in the presence of GRs. The toxicity of TBBPA can be greatly decreased after debromination. However, the total organic carbon is not decreased as no mineralization occurs during debromination by GR. The debrominated TBBPA is less toxic and much easier to be degraded/mineralized microbially. The modification of GR by zero-valent Cu NPs can greatly

Fig. 9 Oxidation products of GR(Cl)–Cu NPs after reaction with TBBPA.

Fig. 10 Proposed debromination pathway for TBBPA removal by GR(Cl)–Cu NPs.
enhance the reductive debromination of TBBPA, and the engineered GR can thus be used as a potential remediation reagent for TBBPA removal.

4. Conclusion

GRs interlayered with Cl\(^{-}\), SO\(_4\)\(^{2-}\), and CO\(_3\)\(^{2-}\) can reduce TBBPA with tri-BBPA, di-BBPA, mono-BBPA, and Br anions as reduction products. GR modified with Cu NPs was found to be more reactive compared to the traditional Cu\(^{2+}\) modification. The optimum Cu NPs content in GR(Cl)–Cu NPs was 0.5%, which showed the highest reactivity toward TBBPA reduction. High pH did not favor TBBPA reduction in both the GR(Cl) and GR(Cl)–Cu NPs systems. The presence of SO\(_4\)\(^{2-}\) and CO\(_3\)\(^{2-}\) inhibited TBBPA reduction by GR(Cl) and GR(Cl)–Cu NPs, and the inhibition effect of PO\(_4\)\(^{3-}\) and humic acid were much greater than SO\(_4\)\(^{2-}\) and CO\(_3\)\(^{2-}\). TBBPA reduction by GR(Cl)–Cu NPs could be explained by a galvanic cell model, whereby electrons are transferred from GR(Cl) to Cu NPs, where TBBPA reduction occurs. Our findings demonstrated that natural-occurring Fe-bearing minerals may play an important role in the reductive transformation of TBBPA besides the biotransformation and that GR(Cl)–Cu NPs can be used for the efficient removal of reducible halogenated pollutants.

Conflicts of interest

There are no conflicts to declare.

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