Simultaneous removal of arsenate and arsenite by a nanostructured zirconium–manganese binary hydrous oxide: Behavior and mechanism

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Arsenate
Arsenite
Adsorption
Oxidation

1. Introduction

As extensively reported, the pollution of arsenic in groundwater is a worldwide problem and most notably in Chile, China, Bangladesh and India [1–6]. Due to its high toxicity and carcinogenicity, the World Health Organization (WHO) has set a stringent limit of 10 μg L−1. As in drinking water aiming at minimizing the health risks.

As(V) and As(III) generally occur in groundwater simultaneously and the latter is the dominant species. As(III) is much more toxic, soluble, mobile, and difficult to remove than As(V). Therefore, pretreatment for As(III) oxidation is usually involved to achieve higher arsenic removal using traditional techniques. Adsorption is considered to be the most promising technology for arsenic removal from groundwater because of high efficiency and cost-effectiveness [12–17]. Thus, developing economical, effective, and reliable sorbents capable of removing both As(V) and As(III) simultaneously from contaminated drinking water is very important.

A series researches [3,6–8] has been conducted on the adsorptive removal of As(V) and As(III) with iron(III) (hydr)oxides, due to their high affinity toward inorganic arsenic species and low cost.

As(III) removal is usually not as effective as As(V) removal for these adsorbents at concentrations normally found in natural water. TiO2 was also extensively reported using as sorbent and/or photocatalyst for removal of arsenic from water [9–11]. Additionally, zirconium-based sorbents gain more attentions since they have remarkable selectivities to arsenic and high resistance against attacks by acids, alkalins, oxidants, and reductants [12–14].

Recently, the development of composite sorbents containing two or more metal oxides is gaining considerable attentions, since the composites not only can inherit the advantages of parent oxides but also show obviously synergistic effect. A Fe–Mn binary oxide adsorbents demonstrated a greater enhancement in both As(V) and As(III) removal [16–19]. A nanostructured Zr(IV)–Mn(IV) binary hydrous oxide sorbent was recently developed by a simple chemical coprecipitation method in our laboratory. The prepared Zr–Mn binary oxide exhibited high adsorption capacity toward both As(V) and As(III) and was much more effective for As(III) removal than As(V). Although sorption characteristics of arsenic by single-component Zr or Mn hydr(o)oxides have been studied and reported, little information is available about the sorption behaviors of Zr–Mn binary hydrous oxide.

Multi-component sorbents often exhibit different sorption behaviors compared to single-component sorbents [20,21]. It is believed that the differences in physical–chemical properties between multi- and single-component solids are the primary reason for the differences in sorption behaviors.
In this study, the sorption characteristics of both As(V) and As(III) by prepared nanostructured Zr–Mn binary hydrous oxide were investigated. Several important studies on adsorption behaviors and mechanisms were performed. The roles of few components in the sorbent on the arsenic removal were discussed; the possible mechanisms involved in arsenic uptake were addressed.

2. Materials and methods

2.1. Materials

All chemicals are analytical graded and were used without further purification. Reaction vessels (glass) were cleaned with 1% HNO3 and rinsed several times with deionized water before use. As(V) stock solution was prepared with deionized water using NaHAsO3·7H2O and As(III) stock solution was prepared with NaOH solution using As2O3. Arsenic working solutions was freshly prepared by diluting arsenic stock solution with deionized water.

2.2. Synthesis of nanostructured Zr–Mn binary hydrous oxide

The Zr–Mn binary hydrous oxide with a molar ratio of 1:1 was prepared by a one-step simultaneous oxidation and coprecipitation method. Mn(VII) salt was first dissolved in deionized water (DI water) and then Mn(II) salt and zirconium salt were dissolved in DI water. Under vigorous magnetic-stirring, the Mn(VII) solution just prepared was slowly added into the second solution, leading to the formation of particles. The suspension was continuously stirred for 1–2 h, aged at room temperature for several hours, and then washed repeatedly with the DI water. The suspension was filtrated and dried at 50°C for 24 h. The dry material was crushed and stored in a desiccator for use. Pure hydrous ZrO2 and MnO2 were also synthesized by similar approach.

2.3. Characterization

The composition of the prepared Zr–Mn binary hydrous oxide was determined by classical chemical analysis. A definite amount of the oxide was treated with 10% oxalic acid solution. The oxide was reduced and dissolved by the oxalic acid and formed Mn2+ and Zr4+ into solution. The content of Mn2+ and Zr4+ in the solution was determined using an ICP-AES (Optima 7300 DV, Perkin Elmer Co. USA).

The specific surface area was measured by nitrogen adsorption using the BET method with a surface area analyzer (Nova 2000e, Quantochrome Instruments, USA). The particle shapes were observed using a field scanning electron microscope (FESEM) (Hitachi S-4800, Japan) and a high-resolution transmission electron microscope (JEOL JEM 3010, Japan). X-ray diffraction (XRD) analysis was carried out on a Rigaku D/MAX-3A diffractometer using Ni-filtered Cu Kα1 radiation.

Several sorbents with and without adsorption of arsenic were prepared and used in the Fourier transform infrared (FTIR) and XPS testing. In the preparation, the pH 7.0 of the solution was maintained by intermittent addition of dilute HNO3 or NaOH; the initial arsenic concentration ([As]0) was 0.133 mM and the sorbent concentration (m) was 200 mg L−1.

The FTIR spectra of Zr–Mn binary oxide before and after treatment with arsenic solution were collected on a FTS-135 spectrometer (Bio-Rad, USA) by transmission model. Samples were ground with spectral grade KBr in an agate mortar. A fixed amount of sample (1%w/w) in KBr was used to prepare the pellet. All IR measurements were carried out at room temperature.

The surface analyses of the Zr–Mn binary hydrous oxide before and after arsenic treatment were conducted using X-ray photoelectron spectroscopy (Kratos XPS System-AXIS His-165 Ultra, Shimadzu, Japan). The XPS spectra were obtained with monochromatized Al KR X-ray source (1486.71 eV) working at 150 W, 15 kV, and 10 mA and base pressure of 3 × 10−8 Torr in the analytical chamber. For wide scan spectra, an energy range of 0–1100 eV was used with pass energy of 80 eV and step size of 1 eV. The high-resolution scans were conducted according to the peak being examined with pass energy of 40 eV and step size of 0.05 eV. The carbon 1s electron binding energy corresponding to graphitic carbon at 284.6 eV was used as reference for calibration purposes. XPS data process and peak fitting were performed using a nonlinear least-squares fitting program (XPSpeak software 4.1).

2.4. Sorption experiments

Sorption isotherms on the Zr–Mn binary hydrous oxide were conducted to estimate the maximum sorption capacity. The experiments were performed at pH 5.0, which was adjusted with 0.1 M of NaOH and HNO3. Initial arsenic concentration varied from 5 mg L−1 to 40 mg L−1. In each test, 10 mg of the adsorbent sample was loaded in the 100-ml glass vessel and 50 ml of solution containing differing amounts of arsenic was then added to the vessel. NaN3O3 was added to present ionic strength (I) that exists in water and wastewater, due to the presence of inert ionic substances (e.g., sodium ions). The vessels were shaken on an orbit shaker at 200 rpm for 24 h at 24 ± 1°C. All samples were then filtered by 0.45 μm membrane filters and analyzed for arsenic and sulfate.

To determine the relationship between arsenate sorption and sulfate release, another isotherm experiment was carried out at pH 4.8. The solution pH was maintained using a buffer of 5 mM sodium acetate.

Sorption envelopes of arsenate and arsenite on Zr–Mn binary oxide were obtained using batch tests. In each test, 10 mg of the adsorbent sample was loaded in the 100-ml glass vessel containing 50 ml of arsenic solution. The pH values of individual samples were adjusted every 4 h with dilute HNO3 and/or NaOH solution to designated values in the range of 3–12 during the shaking process. The equilibrium pH was measured and the supernatant was filtered through a 0.45 μm membrane after the solutions were mixed for 24 h.

2.5. Analytical methods

Total arsenic (As(III) + As(V)) and sulfate concentrations were, respectively, determined using an inductively coupled plasma atomic emission spectroscopy machine (ICP-AES, Optima 7300 DV, Perkin Elmer Co. USA). Prior to analysis, the aqueous samples were acidified with concentrated HNO3 in an amount of 1% and stored in acid-washed glass vessels. The experimental error <5% was controlled.

3. Results and discussion

3.1. Properties of Zr–Mn binary hydrous oxide

The chemical analysis of synthesized Zr–Mn binary oxide shows that the Zr/Mn molar ratio of the bulk is 0.971 ± 0.02 and the Zr, Mn, and sulfate content is about 27.9%, 17.4% and 9.6%, respectively. No obvious crystalline peak is observed from the XRD pattern of Zr–Mn binary oxide, indicating that both Zr oxide and Mn oxide exist mainly in amorphous form. The amorphous Zr–Mn binary oxide has a high BET surface area of 213 m2 g−1. Fig. 1a illustrates the FESEM images of the Zr–Mn binary oxide particles which demonstrates that they are micro-sized grains (2–35 μm) aggregated with smaller nanosized particles, resulting in a rough
surface and the presence of porous structure. The TEM image (Fig. 1b) shows that the average size of nanoparticles is around 100 nm, with nonuniform shapes. The analysis of XPS results (demonstrated in Fig. SI1) reveals that both zirconium and manganese in the synthesized sample are mainly in the oxidation state of +IV. This indicates that the sorbent could be effectively oxidizing As(III) to As(V) since MnO₂ is an effective oxidizing agent of arsenite [22,23].

3.2. Sorption isotherms

The sorption capacities of the Zr–Mn binary hydrous oxide for arsenic were evaluated at pH 5.0. As shown in Fig. 2, the Zr–Mn binary hydrous oxide has high sorption capacity for both As(V) and As(III) and is much more effectively for As(III) removal than As(V). Furthermore, it is interesting to note that the presence of As(III) could enhance the total arsenic uptake when we compare the sorption behaviors of the three cases. Similar phenomena were reported on the Mn-based sorbents [17,24,25]. It is possible that the reductive dissolution of manganese dioxide causes an increase in fresh sorptive sites for arsenic at the solid surface during As(III) oxidation, leading to an increase in formed As(V) removal.

Both Langmuir and Freundlich equations were employed to describe the sorption isotherm data. As shown in Table 1, higher regression coefficients suggest that the Langmuir model is more suitable for describing the sorption behavior than Freundlich model.

Direct graphic maximal sorption capacity (corresponding to the isotherm plateau) gives maximal capacities of 80 and 104 mg g⁻¹ for As(V) and As(III), respectively. These qmax values are compared with the reported values of other sorbents (Table 2). It is found that the prepared Zr–Mn binary hydrous oxide outperforms many other

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Table 1

<table>
<thead>
<tr>
<th>As species</th>
<th>Langmuir model</th>
<th>Freundlich model</th>
</tr>
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<tr>
<td></td>
<td>qmax (mg g⁻¹)</td>
<td>b (L mg⁻¹)</td>
</tr>
<tr>
<td>As(V)</td>
<td>81.30</td>
<td>4.24</td>
</tr>
<tr>
<td>50%As(V) + 50%As(III)</td>
<td>96.15</td>
<td>2.42</td>
</tr>
<tr>
<td>As(III)</td>
<td>102.04</td>
<td>2.23</td>
</tr>
</tbody>
</table>

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Table 2

Comparison of maximum arsenic adsorption of different sorbents.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Concentration range (mg L⁻¹)</th>
<th>qmax for As(III) (mg g⁻¹)</th>
<th>qmax for As(V) (mg g⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO₂·xH₂O</td>
<td>0.3–100</td>
<td>47.1 (7.0)</td>
<td>29.3 (7.0)</td>
<td>[26]</td>
</tr>
<tr>
<td>MWCNT-ZrO₂</td>
<td>0.1</td>
<td>2.0 (6.0)</td>
<td>5.0 (6.0)</td>
<td>[27]</td>
</tr>
<tr>
<td>MnO₂</td>
<td>0.1–50</td>
<td>9.7 (N/A)</td>
<td>7.5 (N/A)</td>
<td>[25]</td>
</tr>
<tr>
<td>R-MnO₂</td>
<td>0.1–80</td>
<td>52.5 (N/A)</td>
<td>22.5 (N/A)</td>
<td>[25]</td>
</tr>
<tr>
<td>Nano-TiO₂</td>
<td>N/A</td>
<td>59.9 (7.0)</td>
<td>37.5 (7.0)</td>
<td>[9]</td>
</tr>
<tr>
<td>CuO nanoparticles</td>
<td>0.1–100</td>
<td>26.9 (8.0)</td>
<td>22.6 (8.0)</td>
<td>[28]</td>
</tr>
<tr>
<td>Fe-Mn oxide</td>
<td>5–40</td>
<td>132.7 (5.0)</td>
<td>69.8 (5.0)</td>
<td>[17]</td>
</tr>
<tr>
<td>Fe-Zr oxide</td>
<td>5–40</td>
<td>120.0 (7.0)</td>
<td>46.1 (7.0)</td>
<td>[19]</td>
</tr>
<tr>
<td>Zr-Mn binary oxide</td>
<td>5–40</td>
<td>104 (5.0)</td>
<td>80 (5.0)</td>
<td>This study</td>
</tr>
</tbody>
</table>

N/A: not available.

* pH is shown in parentheses.
sorbents. It should be noted that this sorbent still has rather high sorption capacity at very low equilibrium concentration (seen in the enlarged graph in Fig. 2), which indicates that it is much more suitable for real groundwater treatment since As level in groundwater is normally below 100 μg L⁻¹ and the As concentration in treated water should be below 10 μg L⁻¹.

3.3. Arsenic sorption edges

Sorption of arsenic onto Zr–Mn binary oxide as a function of pH from 3 to 11 is shown in Fig. 3. In the pH range of the experiments, As(V) sorption is obviously dependent on pH. It becomes favored at low pH and decreases with an increase in solution pH. In the tested pH range (3–11), H₂AsO₄⁻ and HAsO₂⁻ are main As(V) species in the solution and more negatively charged As(V) species dominate at higher pH. Lower pH is favorable for the protonation of sorbent surface. Increased protonation is thought to increase the positively charged sites, enlarge the attraction force existing between the sorbent surface and As anions and therefore increase the amount of adsorption in the lower pH region. With the increase in solution pH, the negatively charged sites gradually dominate, the repulsion effect enhances, and the amount of adsorption is consequently dropped.

Typically, sorption of As(III) by metal oxides differs obviously from As(V) and usually reaches a maximum at pH values similar to pKₐ of the acid. For the Zr–Mn binary hydrous oxide system, the As(III) sorption edge is almost the same as that of As(V), indicating that initial added As(III) is completely oxidized into As(V) and then sorbed by the Zr–Mn binary oxide.

3.4. Role of sulfate

It is accepted that the replacement of surface hydroxyl groups on metal oxides by anions such as arsenate is mainly responsible...
for their sorptive removal from solution aqueous [29]. Additionally, the exchange between the sulfate ion on the surface and the arsenic ions may play an important role in As(V) uptake [30,31]. The prepared Zr–Mn binary oxide was found to contain about 9.6% sulfate. Thus, the anion exchange between the arsenic and sulfate on the surface of Zr–Mn binary oxide may play a certain role in arsenic uptake.

To investigate the role of sulfate exchange in arsenate sorption, the relationship between the amount of released sulfate and amount of sorbed arsenate was examined with the result shown in Fig. 4. From the slope of the regression line of relatively low coverage, the Zr–Mn binary oxide releases about 0.31 mmol sulfate for every 1 mmol As(V) that is sorbed.

For higher arsenate coverage, the role of sulfate exchange in arsenate sorption is not obvious, since the exchangeable sulfate is almost completed released to the solution. However, this anion exchange is not the main mechanism for As(V) sorption because of the relatively low release ratio of sulfate. Thus, it could be concluded that the replacement of surface hydroxyl groups might be the dominant mechanism for As(V) uptake and sulfate exchange play an important role.

3.5. FTIR and XPS analyses

Infrared Vibrational Spectroscopy (IR) and X-ray Photoelectron Spectroscopy (XPS) are powerful techniques for the study of reactions that occur in various systems (e.g., reduction and adsorption) [32–34]. FTIR spectra of Zr–Mn binary oxide before and after reaction with arsenic are shown in Fig. 5C. For comparison, the FTIR spectra of pure ZrO2 and pure MnO2 before and after reaction with arsenic were collected and are presented in Fig. 5 A and B, respectively.

For ZrO2 spectra, the band at 1625 cm⁻¹ is assigned to the deformation of water molecules and indicated the presence of physisorbed water on the oxide. The peaks at 1566 and 1350 cm⁻¹ might be ascribed to the asymmetric stretching vibration of sorbed CO₂ since the systems are open to atmosphere during the preparation of Zr oxide and KBr pellets [35]. After reaction with As(III), no significant change is observed in the FTIR spectrum while a new band, corresponding to As–O stretching vibration, appears at 832 cm⁻¹ after reaction with As(V). This indicates that the As(V) is bound as a surface complex and not as a precipitated solid phase.

For MnO2 spectra, only a peak at 1625 cm⁻¹, corresponding to the vibration of water molecules, is obviously observed. No obvious change is found for the sample after reaction with As(V) or As(III). This may be due to its low sorption capacity for arsenic.

For original Zr–Mn binary oxide spectra, the peak at 1630 cm⁻¹ is assigned to the deformation of water molecules; the two peaks at 1580 and 1380 cm⁻¹ might be attributed to the vibration of sorbed CO₃²⁻; three peaks at 1122, 1065, and 984 cm⁻¹ could be ascribed to the vibration of sulfate [36]. After reaction with As(V), the

<table>
<thead>
<tr>
<th>Sample</th>
<th>Zr(t) At.%</th>
<th>Mn(t) At.%</th>
<th>O(t) At.%</th>
<th>S(t) At.%</th>
<th>As(t) At.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr–Mn binary oxide</td>
<td>15.17</td>
<td>12.69</td>
<td>69.28</td>
<td>2.85</td>
<td>0.0</td>
</tr>
<tr>
<td>Zr–Mn binary oxide after reaction with As(V)</td>
<td>13.30</td>
<td>13.25</td>
<td>70.13</td>
<td>0</td>
<td>3.32</td>
</tr>
<tr>
<td>Zr–Mn binary oxide after reaction with As(III)</td>
<td>14.55</td>
<td>14.97</td>
<td>68.86</td>
<td>0.07</td>
<td>3.45</td>
</tr>
</tbody>
</table>

Table 3 Compositions of Zr–Mn binary oxide before and after arsenic sorption.

Fig. 6. As3d core level of the sorbed arsenic. (a) after reaction with As(V) and (b) after reaction with As(III). [As]₀ = 10 mg/L; m = 200 mg/L.

Fig. 7. Mn2p core level photoelectron spectra of (a) Zr–Mn binary hydrous oxide, (b) Zr–Mn binary hydrous oxide after reaction with As(V) and (c) Zr–Mn hydrous oxide after reaction with As(III). [As]₀ = 10 mg/L; m = 200 mg/L.
peaks at 1580 and 1380 cm\(^{-1}\) do not obviously change, while three peaks at 1122, 1065, and 984 cm\(^{-1}\) disappear completely and a new peak at 832 cm\(^{-1}\) appears, corresponding to As–O stretching vibration. This suggests that the sulfate on the surface of the oxide might be displaced with arsenate and the appearance of sulfate in the solution also confirms our interpretation. After reaction with As(III), the change in spectra is almost same as As(V), which indicates the conversion of As(III) to As(V) during its uptake.

The surface compositions of Zr–Mn binary oxide before and after reaction with arsenic and valence state of sorbed arsenic were determined by the XPS. The changes in surface compositions are presented in Table 3. After reaction with As(V), the sulfate groups on the surface are completely displaced; the arsenate appears at the solid surface. Similar phenomenon can be observed after the reaction with As(III). However, the Mn atom content increases, which is not anticipated, since the reductive dissolution of MnO\(_2\) should reduce the Mn content during As(III) sorption and oxidation. It is very likely that the released Mn\(^{2+}\) is sorbed onto the solid surface again since the reaction is carried out at pH 7.0; no soluble Mn is detected in the solution.

Fig. 6 shows the As3d core level of the Zr–Mn binary oxide after the adsorption of arsenate (Fig. 6a) and arsenite (Fig. 6b). There is no obvious difference between the As3d spectrum of the Zr–Mn oxide after reaction with As(V) and that after reaction with As(III). The binding energies are 45.3 and 45.2 eV, respectively. Commonly, binding energies of As3d core level for As(III) and As(V) in arsenic oxides are 44.3–44.5 and 45.2–45.6 eV, respectively [34,37]. They can be slowly shifted up to 44.6 ± 0.13 eV for As(III) and 46.0 ± 0.17 eV for As(V) when arsenic anions or molecules are adsorbed onto iron oxide [38]. This indicates that the arsenic species sorbed onto the Zr–Mn binary hydrous oxide after reaction with As(III) is As(V). It is further confirmed that the oxide is effective for As(III) oxidation.

The Mn2p spectra of Zr–Mn hydrous oxide before and after reaction with As(V) or As(III) are shown in Fig. 7a–c, respectively. The binding energy of Mn2p\(_{3/2}\) of original Zr–Mn binary hydrous oxide is 642.03 eV. It was reported that the Mn2p\(_{3/2}\) binding energy of birnessite was 642.0 ± 0.1 eV [39], which suggested that the Mn oxide in the Zr–Mn binary oxide was mainly MnO\(_2\). After reaction with As(V), the binding energy is 642.01 eV and had almost no change, whereas an obvious shift in the binding energy (from 642.03 to 641.66 eV) is observed after reaction with As(III).

This might be ascribed to an increase in the reduced Mn species at the surfaces of the Zr–Mn binary hydrous oxide. Nesbitt and Banerjee analyzed thoroughly the Mn2p spectra of Mn oxyhydroxides and found that binding energies of Mn(IV), Mn(III), and Mn(II) species were very close to each other and the binding energy of Mn with low oxidation state located on the low energy levels [39,40].

3.6. Arsenic uptake mechanisms

It can be concluded that the arsenate uptake is achieved mainly through the replacement of surface hydroxyl groups and sulfate with As(V) anions and formation surface complexes, as described in Fig. 8. It is rather complicated because not only sorption but also surface redox reactions are involved.

As(III) is mainly present in uncharged H\(_2\)AsO\(_4\) species under tested conditions since arsenite has a pK\(_a\) value of 9.2. H\(_2\)AsO\(_4\) molecules are firstly transported to the solid/water interface from bulk solution and are then sorbed onto the surface by formation of inner-surface complex. The H\(_2\)AsO\(_4\) molecules sorbed through formation of As(III)–O–Mn complex transfer two electrons to the Mn atoms, by which As(III) is oxidized into As(V). The formed As(V) and Mn\(^{2+}\) are released into the solution along with the reductive dissolution of MnO\(_2\). New active sorption sites are produced at the solid surface during this process. The As(V) in the solution phase is then transported to the solid/water interface and adsorbed onto the surface, occupying empty sorption sites or replacing the sorbed As(III). The Mn\(^{2+}\) might be also adsorbed to the surface since the surface is negatively charged. This process continues until As(III) or available MnO\(_2\) is depleted.

4. Conclusions

A nanostructured zirconium–manganese binary hydrous oxide is synthesized by a one-step simultaneous oxidation and coprecipitation method. The synthetic Zr–Mn binary hydrous oxide is amorphous and Zr and Mn in this oxide exist mainly in the oxidation state +IV. The Zr–Mn binary hydrous oxide particles are aggregated with smaller nanosized particles, resulting in a rough surface and high BET surface area of 213 m\(^2\) g\(^{-1}\). The nanoparticles could effectively oxidize As(III) to As(V) and greatly remove both As(V) and As(III). The maximal sorption capacities of As(V) and As(III)
were 80 and 104 mg g$^{-1}$ at pH 5.0, respectively. Both As(V) and As(III) sorption are strongly pH dependent and are decreasing with an increase in pH value. As(V) uptake may be mainly achieved through replacement of hydroxyl groups and sulfate anions on the surface of the oxide and formation of inner complexes. While the As(III) removal is a sorption couples with oxidation process, in which MnO$_2$ content is mainly responsible for oxidizing As(III) to As(V), which is adsorbed onto the ZrO$_2$.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcis.2012.11.056.

References