



# Rapid degradation of atrazine by hydroxyl radical induced from montmorillonite templated subnano-sized zero-valent copper



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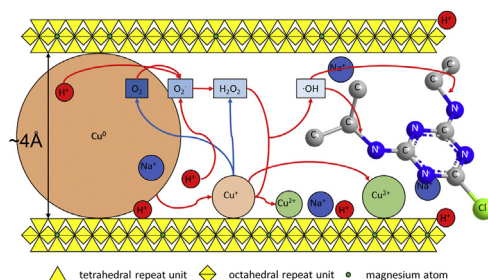
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## HIGHLIGHTS

- Sub-nano sized Cu<sup>0</sup> was synthesized in the confined space of montmorillonite clay.
- Molecular oxygen can be activated by clay-templated Cu<sup>0</sup> to form hydroxyl radical.
- Clay-templated Cu<sup>0</sup> shows superior reactivity to degrade atrazine.

## GRAPHICAL ABSTRACT



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## ABSTRACT

In this study, subnano-sized zero-valent copper (ZVC) was synthesized using montmorillonite clay mineral as the template. The discrete distribution of surface charge on montmorillonite effectively separates the formed ZVC particles and inhibits their aggregation. X-ray diffraction result indicates that the size of ZVC particles on montmorillonite is ~6 Å, which is much smaller than nano-ZVC prepared by conventional method. The montmorillonite templated ZVC (ZVCMMT) shows superior reactivity as indicated by the degradation of atrazine, over 90% atrazine (15 μM) could be degraded in a few min. Hydroxyl radical is confirmed as the reactive species, which is produced from the activation of oxygen by ZVC. It was also shown that the degradation process is strongly dependent on the hydration status of synthesized ZVCMMT. The freeze dried ZVCMMT exhibits higher reactivity compared to freshly prepared ZVCMMT, which can be explained by the higher adsorption of atrazine and oxygen residue on freeze dried ZVCMMT surface. In addition, the toxicity of atrazine is significantly decreased after the reaction with ZVCMMT, indicating that ZVCMMT could be used as a promising material for rapid remediation of persistent organic contaminants.

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## 1. Introduction

Due to the strong reductive activity, zero-valent metals (ZVMs)

have been extensively studied and widely used for environmental remediation of various heavy metals and organic contaminants (Ponder et al., 2000; Dries et al., 2005; Jacqueline et al., 2005). It has been shown that ZVMs can effectively reduce chromate (VI) (Liu et al., 2008), nitro-aromatic compounds (Gu et al., 2010), and chlorinated organic chemicals (Pearson et al., 2005) under anaerobic conditions. However, recent studies reveal that ZVMs could also induce Fenton-like reactions to eliminate organic pollutants by

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activating the molecular oxygen (Joo et al., 2004; Englehardt et al., 2007; Katsoyiannis et al., 2008; Keenan and Sedlak, 2008a, b). For instance, in the case of zero-valent iron (ZVI), the reaction is initiated by a two-electron transfer from ZVI to the oxygen adsorbed on its surface and forms a reduced oxygen anion ( $O_2^-$ ), which could subsequently protonate and finally generate hydrogen peroxide ( $H_2O_2$ ) in the presence of free protons (Keenan and Sedlak, 2008a). It was also reported that  $H_2O_2$  could be produced through a one-electron transfer process by reaction between ferrous iron and oxygen (Huang et al., 2002; Kim et al., 2015). The formed  $H_2O_2$  can be further decomposed into hydroxyl radical ( $\cdot OH$ ) catalyzed by  $Fe^{2+}$ , and  $\cdot OH$  is considered as one of the most reactive species to oxidize many organic contaminants (Buxton et al., 1988).

Among the ZVMs, ZVI is most studied. Due to the strong reduction potential, especially under acidic conditions, ZVI can be consumed by free protons to form  $H_2$  directly (Wang et al., 2014), which might limit the usage of ZVI at low pH. However, as protons are necessary to dismutate  $\cdot O_2^-$ , low pH would be essential for the production of  $H_2O_2$  (Keenan and Sedlak, 2008a). Therefore, it is desirable to find other ZVMs to overcome the drawbacks of ZVI. Copper has a standard reduction potential of 0.34 V ( $Cu^{2+}/Cu$ ) (Gang et al., 2014), which would prevent the reaction with protons via displacement reaction to produce  $H_2$  gas. Thus this renders zero-valent copper (ZVC) as an alternative for ZVI.

Currently, only a few researches have been conducted to investigate the reactivity of ZVC. A prior study showed that ZVC could effectively degrade azo dyes by activation of molecular oxygen to produce  $Cu^+$  and  $\cdot OH$ , leading to the cleavage of  $N=N$  bonds of the azo dyes through a Sandmeyer reaction under neutral pH and aerobic conditions (Dong et al., 2014). The results from Gang and his co-workers (Gang et al., 2014) indicated that ZVC exhibited higher persistent oxidation capacity compared to ZVI, zero-valent aluminum and zero-valent zinc as indicated by the oxidative degradation of diethyl phthalate.

Due to the high surface area and reactivity, nano-sized ZVC (nZVC) was synthesized by various methods. For example, nZVC can be formed by addition of  $NaBH_4$  to reduce  $Cu^{2+}$  to  $Cu^0$ , and the average diameter is about 50 nm (Huang et al., 2012). A solvothermal method was also developed to synthesize nZVC with the diameter of  $\sim 30$  nm (Dong et al., 2014). It is well known that nanoparticles tend to agglomerate, which diminishes their reactivity. Hence, different strategies have been employed to stabilize the formed nanoparticles. Stabilizers such as carboxylic acids and polyvinyl alcohol (Khanna et al., 2007), oleylamine (Dadgostar et al., 2010), and poly amidoamine dendrimers (Balogh and Tomalia, 1998) have been used to disperse copper nanoparticles. Whereas, these stabilizers are all organic chemicals, which might interfere with the reactive oxygen species (ROS) generated from the activation of oxygen by ZVC.

Montmorillonite is a common clay mineral widely distributed in soils, subsoils and sediments (Gu et al., 2008). As a natural nanomaterial, the size of elementary platelet of montmorillonite is a few tens to hundreds of nanometers wide and 1–1.8 nm thick (Pinnavaia, 1983; Laszlo, 1987). Our previous studies showed that montmorillonite could be used as a template to synthesize subnano-sized ZVI (Gu et al., 2010; Zhang et al., 2015). With the unique structure of montmorillonite, ZVI was formed in the constrained interlayer region of montmorillonite with average size of 0.5 nm. The montmorillonite template ZVI showed higher reactivity and efficiency compared to other forms of ZVIs (Gu et al., 2010). Therefore, it is expected that highly reactive nZVC could also be formed with montmorillonite as the supporting matrix.

Atrazine was used worldwide as the herbicide since 1958 and has been banned in the European Union in 2004 due to its highly persistent nature in the environment. It has been reported that the

concentration of atrazine could reach  $0.068 \mu g L^{-1}$  in groundwater even after 21 years since its last application (Vonberg et al., 2014). Atrazine can cause chronic prostatitis (Stanko et al., 2010) and mammary gland development problems in Long-Evans rats after a prenatal exposure (Enoch et al., 2007). It also can cause algae death after an acute exposure (Ralston-Hooper et al., 2009). Recently, numerous methods have been developed to remove atrazine through oxidation (Guan et al., 2013; Hu and Cheng, 2014), reduction (Stephen et al., 1998) and biological degradation (Ghosh and Philip, 2004).

In this study, a new method to synthesize nZVC was developed using natural montmorillonite as the support and the degradation process of atrazine by this montmorillonite templated nZVC (ZVCMMT) through a Fenton-like reaction was investigated without addition of  $H_2O_2$ . The results clearly demonstrate that the isolated distribution of exchangeable  $Cu^{2+}$  effectively separates the nZVC nanoparticles and prevents their aggregation upon the reduction by  $NaBH_4$ . With the smaller particle size (6 Å), ZVCMMT exhibits exceptional reactivity for the decomposition of atrazine under acidic conditions, as the initial degradation rate increases 27 and 13 times compared to commercial available ZVC ( $\sim 20$  nm) and nZVC ( $\sim 25$  nm) prepared by conventional method, respectively. Our results also indicated that the degradation process is strongly affected by the hydration status of ZVCMMT. Freeze dried ZVCMMT showed higher reactivity than the freshly prepared, which may be explained by the higher adsorption of atrazine and residual oxygen on the surface of dried clay minerals.

## 2. Materials and methods

### 2.1. Chemicals

Atrazine (99.1%) and its metabolites (atrazine-desethyl (DEA), 99.5%; atrazine-desisopropyl (DIA), 97.5%; atrazine-desethyl-desisopropyl (DEDIA), 96.3%), and atrazine standard solution ( $101 \text{ ng } \mu L^{-1}$ , dissolved in methanol) were obtained from Fluka (Ronkonkoma, NY, USA). Xanthine, xanthine oxidase, sodium borohydride, copper chloride dihydrate, zero-valent copper powder (spheroidal) with the average diameter size of 20  $\mu m$  and 5,5-dimethyl-1-pyrrolone *N*-oxide (DMPO) were all purchased from Sigma-Aldrich. Methanol and acetonitrile were of HPLC grade and from Merck (Darmstadt, Germany). All the chemicals were used as received without any further purification.

### 2.2. Preparation of ZVCMMTs and nZVC

Montmorillonite clay mineral used in this study was obtained from Fenghong Chemical Co. (Zhejiang Province, China) with the measured cation exchange capacity (CEC) of  $77 \text{ cmol kg}^{-1}$ . The preparation of ZVCMMT followed the method of Gu and his co-workers (Gu et al., 2010). Briefly,  $Na^+$ -montmorillonite was initially exchanged with cupric ion ( $Cu^{2+}$ ) by simply saturating the clay mineral using 0.1 M  $CuCl_2$  solution. Copper content in clay mineral was determined by a flame atomic absorption spectrometry (Thermo fisher, M6, USA) after digestion with a mixture of hydrofluoric and hydrochloric acid. Then, the pH of the  $Cu^{2+}$ -montmorillonite slurry was adjusted to  $\sim 2$  using 1 M  $HClO_4$  before addition of  $NaBH_4$  with the molar ratio of  $NaBH_4/Cu^{2+} = 30$ . Finally, the clay suspension was washed with oxygen free water to remove the excess of  $NaBH_4$ . For each experiment, ZVCMMT was freshly prepared. In addition, a portion of ZVCMMT was freeze dried to investigate the effect of hydration status on the degradation of atrazine, which was then stored in a desiccator with nitrogen gas atmosphere. Montmorillonite templated zero-valent iron (ZVIMMT) was also prepared following the same procedure as

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