Ultra-low concentration of total organic carbon in ultrapure water using ion-exchange resin embedding silanized magnetic nanoparticles

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Abstract

Regeneration of pure water is an important issue not only for the healthy life but also for the fine control of precise processes in various industries. One important issue in ultrahigh purified water is to reduce the amount of total organic carbon (TOC). Herein, we introduce a new approach to reduce the TOC using the surface silanized nanoparticles, in which the magnetic nanoparticles (mNPs) are silanized and then complexed with ion-exchange resin (IER) beads. The Fe₃O₄ mNPs are surface modified by using high concentrated vinyltrimethoxysilane (VTMS) and then adhered on the surface of IER beads. The surface modified mNPs have a thick-shell of polysiloxane layer varying from 5 to 22 nm depending on the amount of VTMS used, which leads the significant increase of specific surface area. The IER beads embedding VTMS-silanized mNPs achieves about 7 mg/L of the TOC level in ultrapure water system, which is two orders less than 228 mg/L of the feeding water and one order less than 96 mg/L from the system using pristine IER beads. This result is mainly attributed to the polysiloxane layer forming broccoli-like surface structure and some part by the vinyl group of VTMS exposed to the amines in the water.

Introduction

Pure water regeneration from the contaminants is an important issue not only for the environmental life cycle and healthy life but also in the various high-tech industries (Worm et al., 2017; Haward, 2018; Romera-Castillo et al., 2018). For decades, the demand of high-purified water in the cutting-edge technology has led the development of ultrapure water (UPW) system. However, the organic carbons affecting the ultrafine control of the UV lithography process of semiconductor and the quality of pharmaceutical chemistry (Jenkins et al., 1996) still remain enough to disturb the fine process in the purified water even after passing through the UPW system (Godec, 2003; Rydzewski and Godec, 2018). This makes the total organic carbon (TOC) level to be usually used as a non-specific indicator of water quality (Nelson and Sommers, 1996). Especially, in the semiconductor process
using the deep UV for the ultra-fine pattern, an ultra-low TOC level (1 μg/L) is requested (Libman et al., 2015; Lee et al., 2016; Rydzewski and Godec, 2018). To meet this need, the most recent UPW systems have adopted a complex combination of various materials and techniques: ion-exchange resins (Humbert et al., 2005), activated carbon (Lambert et al., 1996), reverse osmosis (Malaeb and Ayoub, 2011), ozonation (Am Water Works Res et al., 1991), ultraviolet light (Legrini et al., 1993), and so on. Nevertheless, it still needs further enhanced techniques and materials or simple process to reduce the TOC level.

There are two major sources of TOC in the purified water when ruling out the contaminants from the transportation system and containers (Godec, 2003). One is the surface water that cannot be controlled from the feeding of TOC and the other is the ion exchange resin (IER) always used for UPW system (Lee et al., 2016). While most of TOC in surface water can be purified by the pretreatment system, the TOC from IER using for the reduction of the organic and inorganic molecules is difficult to control. Since IER is made by organic polymers with active functional groups, for example, sulfonic acids from cation resins and amines from anion resins (Reichenberg, 1953; Sahu and Jaiswani, 2018), the trace contaminants from IER are inevitably released. Recently, the combination system of mixed IER bed, UV oxidation and reverse osmosis has been used to enhance the efficiency of TOC reduction (Lee et al., 2016). Meanwhile, among the TOC originated from the chemical degradation of IER, trimethylamine (TMA, anion resin), benzenesulfonylic acid (cation resin), urea (source water), tetramethylammonium hydroxide (TMAH, reclaim water) are unsatisfactorily removed by the normal systems (Rydzewski and Godec, 2018). Although new materials such as graphene, carbon materials and cellulose nanofiber have been rigorously studied to reduce the contaminants, they are not widely used yet because of the cost effectiveness and the potential environmental toxicity (Apul et al., 2013; Das et al., 2014; Smith and Rodrigues, 2015). Polymer-metal hybrid structures have been introduced as an alternative material for reducing the hazardous chemicals in water (Samiey et al., 2014), but, most of polymer-metal hybrid structures were used for inorganic ion capture (Lee et al., 2003) or for specific organic molecules such as Methyl Orange and phosphate (Wang et al., 2012). On the while, from past few decades the magnetic nanoparticles (mNPs) have been studied as a sorbent due to the facilitation of sorbent-liquid separation, a high surface area and the utilities of surface modification (Ambashta and Sillanpää, 2010). The mNPs embedded IER or surface functionalized mNPs were used for organic and inorganic pollutants like fluoride, polycyclic dyes and heavy ions. However, so far, it has not been much studied the mNPs for the reduction of TOC, especially amines in the ultrapure water.

In this work, we fabricated a highly silanized mNPs hybridized with IER microbeads to reduce the TOC in the ultrapure water. The core-shell like mNPs fabricated through the silanization using vinyltrimethoxysilane (VTMS) (VTMS-mNPs) were examined by the surface characterization methods. After adhering the VTMS-mNPs on the surface of IER beads (h-IER), we applied them to the water purifying system. Also, we briefly discussed the reduction mechanism of TOC with the h-IER.

1. Materials and methods

1.1. Materials

Magnetic nanoparticles (Fe₃O₄), vinyltrimethoxysilane (VTMS) and sodium dodecyl sulfate (SDS) were purchased from Sigma-Aldrich. Ion exchange resin (IER) was obtained from Samyang Co., LTD. Aqueous ammonia (28%, extra pure reagents), ethanol (ACS grade) were purchased from Yakuri pure chemicals and Honeywell Co., LTD, respectively. All the chemicals were used as received without further purification.

1.2. Silanization and hybridization of magnetic nanoparticles (VTMS-mNPs)

0.2 g of SDS was dissolved into 200 mL of ethanol in a three-necked flask. Then, 10 g of Fe₃O₄ nanoparticles were added to the solution. The mixture was sonicated for 30 min in an ultrasonic bath and then stirred at room temperature (25°C). VTMS and 10 mL of aqueous ammonia were sequentially added to the mixture depending on the various concentrations of VTMS. Finally, the mixture was stirred for 24 h at room temperature (25°C). After that, the vinyl functionalized silica-coated Fe₃O₄ nanoparticles were thoroughly washed with ethanol and deionized water and vacuum dried. IER and VTMS-mNPs were mixed at a volume ratio of 95:5 (a total volume = 100 mL) in deionized water. For the better hybridization, the mixture was sonicated for 30 min. After that, the composite was washed thoroughly washed with deionized water and vacuum dried.

1.3. Characterization and measurements

The morphology of the vinyl functionalized mNPs and its hybrid with IER were measured by scanning electron microscope (SEM) (JEOL/JSM-6701f). Shell thickness of VTMS-mNPs was estimated from the high resolution-transmission electron microscope (HR-TEM) (JEOL/JEM-3010) images. The silation of mNPs was examined by Fourier-transform infrared spectroscopy (FT-IR) (Thermo/NICOLET6700), attenuated total reflection (ATR)-FTIR and zeta potential measurement. Specific surface area of VTMS-mNPs was measured by BET surface area analyzer (micromeritics/ASAP2010). The ratio of VTMS-mNPs to IER in the hybrid was analyzed thermogravimetric analyzer (TGA) (PerkinElmer/Pyris1TGA). Total organic carbon (TOC) of feed in and feed out water from test beds was measured by Anatel A1000 TOC analyzer.

2. Results and discussion

2.1. Silanization and hybridization process of VTMS-mNPs with IER beads

Appropriate introduction of the functionalized mNPs into IER can take many advantages without being afraid of the hazard of nanoparticle (Zhao et al., 2011; Sarkar et al., 2012). The hybridization pathway between nanoparticles and IER can be roughly classified into two: (1) dispersing or physically
absorbing the nanoparticles to the polymer IER, (2) grafting on the polymer chains or in situ polymer-assisted growth of nanoparticles while synthesizing IERs. While the latter is for the composite-like structure that the mNPs are fully embedded into IER beads, the former exposes nanoparticles to water. To effectively uptake the advantages of surface silanized mNPs for water purification, it is better that they are directly exposed to water. Accordingly, in this experiment we adapted the former method together with a robust hybridization of silanized mNPs to the surface of IER beads. Fig. 1a shows the brief experimental process classified into two steps for convenience. The first step (Step 1) shows the silanization of mNPs using VTMS, where the light blue represents the shell-like layer of silanized VTMS. The chemical structure is a vinyl group exposing to the outside. The second step (Step 2) shows the hybridization of VTMS-mNPs with IER beads, in which the IER beads is several hundred micrometers that is about three orders larger than that (100 nm) of mNPs. It is noted that in the practical experiment these two steps are consecutively processed. Fig. 1b shows the digital images of h-IERs after completing the hybridization process. Depending on the ratio of VTMS (volume of VTMS/gram of mNPs), the color of h-IER changes and becomes yellowish close to the pristine of mNPs regardless of the VTMS ratio. However, it appeared the flocculation of mNPs when the VTMS was silanized on the surface of mNPs. This is confirmed by TEM images (Fig. 2a, bottom). In the TEM images, the aggregation of mNPs could be more easily observed in the mNPs using higher ratio of VTMS. Moreover, as the ratio of VTMS increases, the shell-like layer becomes clear that can be obviously seen in the set of TEM images. Fig. 2b is the plot of shell thickness increment as a function of VTMS ratio. The shell thickness becomes increase from 5 to 22 nm when the ratio of VTMS varies from 1.0 to 1.75 mL/g. This demonstrates that the mNPs can have a shell-like layer on the surface through the silanization process in the high concentration of VTMS. Fig. 2c shows the FT-IR spectra of mNPs, VTMS and VTMS-mNPs. There are strong characteristic absorption peaks of VTMS assigned to the vibration of Si–O–CH₃ at 773, 816, 1087 and 1192 cm⁻¹, and the vinyl group (Si–CH=CH₂) at 970, 1010, 1410 and 1160 cm⁻¹. In the spectra from VTMS-mNPs the vibration peaks of Si–O–CH₃ are sharply decreased while the peaks at 1047 and 1137 cm⁻¹ assigned to the stretching vibration of Si–O–Si are appeared and increased according to the amount of VTMS used. Also, the vinyl group related peaks are remained (Ahmed et al., 2009; Hajiali and Shojaei, 2016). However, the trace of the vibration peaks of Si–O were definitely observed compared to the weak peaks at 757 and 840-950 cm⁻¹ and the broad peaks at 1047 and 1137 cm⁻¹. In addition, there is a peak at 1276 cm⁻¹ assigned to the vibration of C–O stretching.

Fig. 1 – Scheme of the synthetic process and VTMS-mNPs images. (a) Step 1: Silanization of Fe₃O₄ magnetic particles using VTMS. Step 2: Tethering VTMS-mNPs on the surface of IER microbead. (b) Digital photographic images of pristine IER, mNPs@IER, and h-IER (1, 1.25, 1.50 mL/g) from left to right.
2.2. Dispersibility and adhesion stability of the h-IER

It is important the dispersibility of the VTMS-mNPs in the water for the successful hybridization of the VTMS-mNPs to the IER beads. When dispersing the VTMS-mNPs in the water, we knew that they were very stable in the water. The dispersibility is related to the electrostatic property of surface of mNPs and Fig. 2d is the zeta potential values of VTMS-mNPs depending on the ratio of VTMS. The zeta potential (ζ) of VTMS-mNPs negatively increased from -8.3 mV of bare mNPs to around -18 mV at 1.75 mL/g of VTMS.

Fig. 3a and Appendix A Fig. S1 show the optical microscope images of h-IER beads, showing that they did not aggregate after the in-situ silanization and hybridization process and the shape h-IER beads was not critically changed compared with the pristine IER. However, the surface morphology of h-IER was obviously changed as can be seen in Fig. 3b and Appendix A Fig. S2 magnifying the area marked by red square in Fig. 3a. In Fig. 3b, the mNPs were well adhered and densely packed on the surface of IER in the low concentration of VTMS. On the while, at higher ratios of VTMS (1.25 and 1.50 mL/g) the number of mNPs was drastically decreased and even hard to be observed. From the comparison of the surface morphology of h-IER before and after the sonication for 30 min in water (Appendix A Fig. S2), mNPs once adhering on the surface of IER were firmly attached. Fig. 3c and Appendix A Fig. S3 show the ATR-FTIR spectra of IER hybridized with mNPs without VTMS and h-IER (1.00 mL/g). From the observed common peaks at 890, 995 and 1029 cm\(^{-1}\) assignable to the signal from \(\text{SO}_3\text{H}\) group and \(\text{N(CH}_3\text{)}_3\), it confirmed that the IER is the mixed cation and anion resin. However, the relative peak intensities at the band around 1350 cm\(^{-1}\) corresponding to amine group and at the bands around 1623 and 1654 cm\(^{-1}\) due to the \(\text{N}^+(\text{CH}_3)_3\text{OH}^-\) suggest that after hybridization, water molecules remaining inside the h-IERs interact with anion groups. This implies that the h-IERs confidently sustain the ion-exchange ability that is the core of IER for the water purification. The weight ratio of VTMS-mNPs to IER beads was evaluated from the selected h-IERs using TGA experiment. Fig. 3d is the comparison of temperature dependent weight loss. The shape of decomposition profiles is similar to that of pristine IER regardless of with or without VTMS-mNPs and the ratio of VTMS, meaning that the hybridization of mNPs or VTMS-mNPs did not affect the thermal stability of IER beads. From the rate of remaining weight, the ratio of VTMS-mNPs to IER beads was estimated and it is listed on Table 1. Compared to the mNPs@IER (4.84 wt%), the ratio of h-IER used 1.00 mL/g of VTMS was increased about 1.63 wt%, however, it was rather decreased to 2.84 wt% in h-IER (1.25 mL/g). This is corresponding to the SEM images shown in Fig. 3b and Appendix A.
Fig. S2 and can be attributed to the adhering number of VTMS-mNPs.

2.3. TOC level testing using the h-IER

After the hybridization, we applied a selected h-IER (1.00 mL/g) to the test bed of UPW system. Fig. 4a shows a simplified test bed filled with h-IER beads. From the left, the pretreated water is fed into the test bed, and then the purified water is fed out in the right. The TOC level of the feeding water was 288–230 µg/L. Fig. 4b shows the comparison of TOC level before and after passing through the test beds. When measuring the TOC level at the water from the test beds filled by pristine IER beads and mNP@IER beads, it was 96 and 93 µg/L, respectively, one order less than that of feed-in water. However, when we used the test bed filled by h-IER (1.00 mL/g), the TOC level of purified water was 6.8 µg/L close to the requested level in the semiconductor industry. This is a remarkable value compared to not only that of feeding water but also those of pristine IER beads and mNP@IER beads. Moreover, it is noticeable that this reduction rate (93%) of TOC by h-IER is achieved only from the first cycle of UPW system.

2.4. Mechanism

It is generally known that the silane molecules form the self-assembled monolayer on the surface under the low concentration. In this work, we have used a strategy that a self-condensation of VTMS under the high concentration can make a thick layer of poly(dimethylsiloxane), especially, on the surface of mNPs (Hajiali and Shojaei, 2016). Of course, this can simultaneously induce the agglomeration of mNPs (Mihara et al., 2009). Our result shows both of a formation of thick layer and an agglomeration of mNPs in Fig. 2a, where the increase of shell thickness as increasing the VTMS ratio. In the comparison of FT-IR spectra (Fig. 2c), the decrease of Si-O-CH₃ vibrational peaks, which is on the contrary to the stretching vibration of Si=O-Si, supports the increase of polysiloxane layer on the surface of mNPs. However, it is noteworthy that there are the weak and broad vibration peaks of Si=O at 757 and 840-950 cm⁻¹ and at 1047 and 1137 cm⁻¹. In addition, it is appeared a peak at 1276 cm⁻¹ assigned to the vibration of C=O stretching. This implies that some of Si=O and methoxy group is still alive on the chain of polysiloxane. Therefore, it can be assumed that the shell structure of mNPs is composed of the oligomeric poly(dimethylsiloxane) and the crosslinking of polysiloxane. This is indirectly supported by the negatively increasing zeta potential (ζ). Because the increment of ζ might be due to the hydrolysis of methoxide group on the oligomeric poly(dimethylsiloxane) and the crosslinking of polysiloxane. The negative ζ consecutively induces the electrostatic repulsion force between particles, resulting into the stable suspension in water. When VTMS-mNPs were hybridized with IER, as the ratio of VTMS increased, the color of h-IER went back to light yellow close to the pristine IER. This indicates the decreasing

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<th>Table 1 – Weight ratio of mNPs on h-IER.</th>
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<td>Pristine IER</td>
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number of absorbed VTMS-mNPs might be due to a small contact area and a negatively increasing $\zeta$. However, once adhering VTMS-mNPs seem to be robustly stick on the surface of IER beads (Appendix A Fig. S2).

The purification efficiency of IER beads is known to depend on porosity, degree of cross-linking, stability, purity, and particle size. ATR-FTIR result in Fig. 3c shows that the ion exchange ability of IER beads was not affected by hybridization. However, the purification performance of h-IER beads was evidently enhanced compared to those of the pristine IER and mNPs@IER, although there was not any proof that the main factors except the particle size were changed by the process. Therefore, we can rationally assume that the reduction of TOC is caused by the thick layer of VTMS on the mNPs. Two mechanisms deserve consideration for the reduction of TOC. One is that the thick layer formed by VTMS silanization enlarges the specific surface area of mNPs, which is affordable to the physical and electrostatically absorption of TOC. Fig. 5 shows a BET measurement result, where a specific surface area increases from 5.9 $\text{m}^2/\text{g}$ of bare mNPs to 19.3 $\text{m}^2/\text{g}$ of h-IER as well as increasing the VTMS ratio. This is an almost 330% increment. The inset Fig. 5 is a magnified surface of VTMS-

mNPs (1.00 mL/g) having a broccoli-like structure. This morphology with wrinkled surface and porous structure due to the randomly silanization of VTMS enlarge the effective surface area of h-IER, must increase the number of exposing active sites of vinyl group that can react with amines, and Si–O and methoxy groups that could not make polysiloxane. Even though the chemical reaction of the amines to the vinyl group of VTMS is occurred with a low possibility, the vinyl group of VTMS is known to capture the TMA, TMAH and urea through the Michael addition (Saidi et al., 2009) and through the interactions and hydroamination due to the methoxide or hydroxide functional group (Anderson et al., 2005). Consequently, this broccoli-like surface would chemically and electrostatically enable the capture of TOC molecules originated from IER and furthermore, might prevent the second contamination.

3. Conclusion

In this study, mNPs were excessively silanized and combined with IER and applied to the UPW system, the TOC level was greatly reduced from 228 to 7 $\mu$g/L, the level needed for the deep UV process in the semiconductor industries. This is due to the excessive silanization of mNPs, which results in the formation of a structure with a very large specific surface area such as broccoli shape on the surface of mNPs, which allows more TOCs to be adsorbed in water. The IER and VTMS-mNPs composite not only dramatically reduces TOC level for capturing of organic molecules including the secondary pollutants from IER in water, but also has various advantages such as easy separation, washing and loss minimization of IER beads during the recycling process.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jes.2019.11.023.

REFERENCES


