Research on recycling of drinking water treatment residuals in environmental remediation: The past and future

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Abstract:

Drinking water treatment residuals (DWTR) is an inevitable by-product generated hugely during potable production. A large volume of DWTR is usually disposed as waste in landfill, leading to high cost. Typically, DWTR is primarily composed of Fe/Al hydroxides, due to flocculants utilization, endowing DWTR with high potential to be developed as adsorbents for many contaminants. It is reasonable to believe that the beneficial recycling of DWTR is a promising strategy for waste management. In the past decade, we investigated the adsorption characteristics and the potential ways for DWTR recycling in environmental remediation comprehensively.

The adsorption characteristics and mechanisms of phosphorus (P), organophosphorus pesticide, heavy metal and hydrogen sulfide by DWTR were determined. Results suggest that DWTR exhibited high adsorption capacity for P. The maximum P adsorption capacity estimated by Langmuir model was 45 mg g^{-1}. P adsorption by DWTR was mainly through ligand exchange, and the adsorbed P was mainly in iron (Fe) bound P and aluminum (Al) bound P. Sequentially heat and acid treatment could increase the P adsorption capability of DWTR significantly. The adsorbed P by DWTR exhibited high stability under different pH (3−9) and dissolved oxygen (DO) levels. In addition, the DWTR was also a multifunctional adsorbent for the removal of organophosphorus pesticide, heavy metal and hydrogen sulfide. The DWTR exhibited a greater affinity for chlorpyrifos (log Koc = 4.76−4.90) and a higher chlorpyrifos sorption capacity (K_F = 5967 $mg^{1-n}\cdot L\cdot kg^{-1}$). The maximum adsorption capacity of DWTR for glyphosate, cadmium (Cd) and cobalt (Co) estimated from Langmuir model was 37.9, 35.4 and 17.3 mg g^{-1}, respectively. DWTR also could effectively remove hydrogen sulfide. Hydrogen sulfide adsorption by DWTR was through oxidization and ligand exchange, and the adsorbed hydrogen sulfide in the DWTR was stable under anaerobic conditions.

The feasibility of DWTR in immobilizing P from wastewater, sediment and soil were confirmed. In wastewater treatment, DWTR could be utilized as substrates in constructed wetlands to remove P from secondary effluent and livestock wastewater. Based on continuous flow and tidal flow constructed wetland for the treatment of secondary effluent, the effective removal of total nitrogen (TN), total phosphorus (TP), chemical oxygen demand (COD) and suspended solids (SS) was achieved at short hydraulic retention times (HRTs) (1–3 d). The treatment of livestock wastewater was conducted in a two stage constructed wetland system: an intermittent aeration constructed wetland and a vertical flow constructed wetlands. The results indicated that the constructed wetland system using the DWTR as substrates could effectively remove contaminant (COD, SS, TN, TP, NH_3-N). The effectiveness and stability of the immobilization capability of DWTR for P in lake sediment was also investigated. P immobilization by DWTR was accomplished through transforming the mobile inorganic P to NaOH extractable P. Under normal pH (5−9), and different conditions of ion strength, organic matter

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content in sediment, redox status, light, microbial activity and sediment re-suspension, DWTR could decrease the potential for P release from sediment significantly, and increase the buffering capacity of sediment for external P loading. An equation was established to calculate the dosage for DWTR to immobilize P in lake sediment. In general, DWTR could control the internal P loading by adsorbing P released from the bottom sediment and immobilizing P in the surface sediment. In addition, DWTR were found to enhance the retention capacity of glyphosate and chlorpyrifos in agricultural soil, reducing the bioavailability of chlorpyrifos and improving the physical and chemical properties of soil (e.g. soil pH and cation exchange capacity).

The potential toxicity of DWTR application was evaluated. Both chemical toxicity and ecotoxicity were assessed. The results showed that DWTR contained various metals, and had relatively high contents of Al and Fe. Different DWTR often had different properties and metals contents and lability, but most of metals in DWTR were largely in stable forms (BCR non-extractable). DWTR also could be considered non-hazardous according to the Toxicity Characteristic Leaching Procedure used in the USA. In most cases, DWTR application had low pollution risks for lake water and sediment, but the lability of Mn in DWTR requires further assessment prior to field application. Application of DWTR could increase the abundance of total bacteria and promote anaerobic ammonium oxidation (anammox) bacteria aggregation in sediment, causing an increase in the activity and diversity of anammox bacteria. In addition, DWTR was nontoxic to aquatic organisms on different trophic levels (*Chlorella vulgaris, Aliivibrio fischeri*) and application of DWTR to control sediment pollution didn’t cause any adverse effect to aquatic organisms.

Overall, our previous studies have shown that DWTR is a potential excellent amendment for immobilizing P in wastewater, sediment and soil. The work on recycling DWTR in environmental remediation has been completed in lab tests, which cannot guarantee similar effects in complex environment. With this regard, the filed-scale studies are ongoing, particularly the contaminants (P, heavy metals, organic pollutants) immobilizing performance and potential toxicity of DWTR being evaluated. Moreover, a new type DWTR is being explored based on DWTR P adsorption characteristics. The modification technology and combined with other materials are being adopted to obtain an ideal P remediation materials. In addition, the DWTR in powder form may lead to clogging in kinds of filtration systems. The low hydraulic conductivity hampers the number of cycles of DWTR. Efforts are needed to develop granular DWTR, and the attempts to granulate DWTR have already been carried out. The preliminary performance evaluation showed that the granular DWTR exhibited strong P adsorption capability and good mechanical stability.

Keywords: drinking water treatment residuals, phosphorus, environmental remediation, environmental risk.

1 Introduction

Drinking water treatment residuals (DWTR) is an inevitable by-product generated in drinking water treatment plant. Typically, DWTR can be classified into coagulant, natural, groundwater or softening, and manganese residuals (Babatunde and Zhao, 2007). Among them, coagulant residuals (referred to as DWTR hereafter) constitute the majority of water treatment plant by-products and have attracted interest for recycling (Ippolito et al., 2011). In the traditional drinking water treatment plant, Al or Fe salts is commonly used as coagulant to remove impurities from raw water. DWTR is thus primarily composed of amorphous Fe/Al hydroxides and together with the removed impurities from the treated water. The quality of DWTR is influenced by the source of drinking water quality, a type of coagulant and the system of treatment plant. DWTR therefore shows a different physico-chemical property but is mainly composed of inorganic matter (Ippolito et al., 2011).

Global for portable water demand has been increasing as the rapid growth of population, resulting in a huge amount of DWTR. The production of DWTR is typically 4-7% by volume of the total water produced (Sun et al., 2015). Within the Europe water industry, annual DWTR production is several million tons (Basibuyuk and Kalat, 2004). The DWTR outputs of Asian countries are also huge. Recent literature documented that 1.5-2.4 million ton dry DWTR generated in China in 2009 (Li et al., 2013); Japan produced 329,628 DS-t of DWTR as dry soil in 2010 (JWWA, 2013); the estimated daily amount of DWTR in Republic of Korea is 1200 tons (ME, 2013); and according to Metropolitan Waterworks Authority (MWA) of Thailand, the DWTR is generated with the maximum capacity of 300 tons per day in the dry season and approximately 700 tons per day in the wet season (Nimwinya et al., 2016). However, little information is available on the global DWTR production. In 1997, Dharmappa et al. (1997) reported that the global daily DWTR production is around 10,000 tons. But, at present, the DWTR production on a global scale is increasing more and more, and exceeds 10,000 tons/day.

The large amount of DWTR is typical disposed as waste via landfilling or discharged into drainage systems without any treatment. The disposal costs of DWTR are likely to increase due to increasing generation of DWTR coupled with environmental restraint on its current disposal outlets. In Ireland, 18,000 tonnes dry solids of alum sludge in an annual basis is generated with landfill disposal costs of about £3.2 million (Hu et al., 2011). The typical cost for DWTR disposal in Netherlands is £30–£40 million per year (Evuti and Lawal, 2011). In addition, in Australia, much of DWTR is disposed to sewer or to landfill with associated total disposal cost of over $6.2 million per annum (Maiden et al., 2015). Hence, the increasing financial and environmental costs have prompted to develop alternative management strategies toward its reuse. In 2004, Japan introduced a water supply service policy (Water Service Vision), which calls for a DWTR recycling percentage increase from 52% (in 2011) up to 100% (Keeley et al., 2016). In some European countries, about 25% of DWTR are mainly reused as component in the manufacture of Portland clinker and in various other industrial sectors (Frías et al., 2014). More than 11 ways, mainly including its used in wastewater treatment process, building and construction, land application, etc., are now being employed in the DWTR reuse processes.

In recent years, recycling of DWTR in environmental remediation has attracted international interest; numerous research studies indicated that DWTR is an ideal adsorbent for various contaminants, including P (Wang et al., 2011), arsenic (Nagar et al., 2010), perchlorate (Makris et al., 2006), hydrogen sulfide (Wang and Pei, 2012), boron (Irawan et al., 2011), mercury (Hovsepyan and Bonzongo, 2009), selenium (Ippolito et al., 2009), cobalt (Jiao et al., 2017), lead (Zhou and Haynes, 2011), chromium (Zhou and Haynes, 2011), copper (Lin et al., 2014), nickel (Chiang et al., 2012), zinc (Chiang et al., 2012), glyphosate (Hu et al., 2011), and chlorpyrifos (Zhao et al., 2013). For P pollution control, DWTR typically serves as the main substrate in constructed wetlands to remove P from wastewater (Babatunde et al., 2009; Babatunde and Zhao, 2009; Zhao et al., 2009; Babatunde et al., 2011; Zhao et al., 2011a; Zhao et al., 2011b; Bai et al., 2014) and as an amendment for in situ remediation of P-contaminated sediments or soils (Agyin-Birikorang and O'Connor, 2009; Wang et al., 2013; Wang and Pei, 2013). Although there are some investigations on potential reuse and recycling of DWTR, comprehensively studies on its recycling in environmental remediation are limited. In the past decade, our group investigated the adsorption characteristics and the potential ways for DWTR recycling in environmental remediation comprehensively. Therefore, in this article, we provided a summary of our recent studies on the application of DWTR for the adsorptive removal of aqueous pollutants (phosphorus (P), organophosphorus pesticide, heavy metal and hydrogen sulfide) and the immobilizing P from sediment and soil. Moreover, its potential toxicity in application processes was also evaluated. Based on the current results, the knowledge gap for future research was proposed.

2 Adsorption characteristics and mechanism of pollutants by DWTR

2.1 P adsorption by DWTR

(1) Adsorption behavior

P adsorption contents of DWTR increased with the initial P concentration. Adsorption kinetics exhibited an initial rapid phase, followed by a slower phase. This could be described by three models, including a pseudo–first-order equation, a pseudo–second-order equation, and a double-constant rate equation. Both the Langmuir and Freundlich isotherms fit the experimental data well, particularly the Freundlich isotherm, which had a correlation coefficient of 0.9930. The maximum measured P adsorption capacity of DWTR was 45.42 mg g^{-1}, which is high when compared to those of most DWTR, as well as other reported adsorbents (Vohla et al., 2011). P adsorption is a spontaneous endothermic process. Highest P adsorption capacities of DWTR were measured at low pHs and a particle size range of 0.6 to 0.9 mm. Both aluminum (Al) and iron (Fe) in the residuals can result in significantly high P adsorption capacities. P was mainly adsorbed in the forms of Al-P and Fe-P. Ligand exchange adsorption is believed to be the major mechanism of P adsorption onto DWTR, and OH^- and organic matter were the dominant ligands. Lower pH values enhanced P adsorption by DWTR. The adsorbed P in DWTR was more easily desorbed under alkaline conditions, however, the amount of P desorption was limited, the adsorbed P by DWTR exhibited high stability under different pH (3−9); and it was also stable under different DO levels. Thus, DWTR can be a reliable P adsorption material.

(2) Effect of the inherent properties of DWTR

Five DWTR were collected from different regions in China, two DWTR were sampled from Beijing (BJ1-DWTR, BJ2-DWTR) and three DWTR were collected from Hangzhou (HZ-DWTR), Lanzhou (LZ-DWTR) and Shandong (SD-DWTR) Province. The five DWTR had variable physicochemical properties. The weight percentage values ranged from 2.5%–9.7% for Fe, 4.2%–9.4% for Al, 0.8%–13% for Ca, 2.9%–10.8% for C, 0.1%–0.3% for P, and 2.6%–6.8% for OM. The maximum P adsorption capacities of the five DWTR calculated using the Langmuir isotherm ranged from 4.17 to 8.20 mg g^{-1} at a pH of 7 and further increased with a decrease in pH. P adsorption capacity of DWTR is affected by its inherent properties. A factor related to Al and 200 mmol/L oxalate-extractable Al (Al_{ox}) accounted for 36.5% of the variations in the P adsorption. A similar portion (28.5%) was attributed to an integrated factor related to the pH, Fe, 200 mmol/L oxalate-extractable Fe (Fe_{ox}), surface area and organic matter (OM) of the DWTR. In addition, the quantity of P desorption was limited and had a significant negative correlation with the (Fe_{ox} + Al_{ox}) of the DWTR ($p < 0.05$). Overall, DWTR with high contents of Al_{ox}, Fe_{ox} and OM as well as large surface areas were proposed to be the best choice for P adsorption in practical applications.

(3) Effect of low molecular weight organic acids

Low molecular weight organic acids (LMWOAs) are distributed widely in nature. The facts that LMWOAs have adverse effects on P adsorption by soil and can also increase the amount of exchangeable Al from soil have been reported (Bolan et al., 1994; Staunton and Leprince, 1996). The concentrations of LMWOAs are usually low in natural environment (Jones, 1998; Strobel, 2001), however, in some special circumstances, they can exist at high levels, which is detrimental to the stability of P in the environment. Thus, the effect of LMWOAs on P adsorption should be assessed. Both batch and column experiments indicated that the effects of LMWOAs on P adsorption were closely related to adsorption time. Initially, all acids presented inhibitory function on P adsorption. The inhibition became weaker with time, eventually promoting P adsorption for citric acid and tartaric acid. In the column experiment with a 61-day duration, high P adsorption rates (>55%) were observed for the test groups containing citric acid and tartaric acid. Interestingly, higher pH likely enhanced P adsorption with the effects of LMWOAs and a distinct relationship between LMWOAs’ effects on P adsorption and their concentrations was not observed. Moreover, fractionation of the adsorbed P from the DWTR demonstrated that oxalic acid reduced P adsorption capacity, while citric acid and tartaric acid increased. Based on the forms of Fe and Al existing in the DWTR and Fourier transform infrared spectroscopy analyses, LMWOAs can promote P adsorption through activating crystalline Fe/Al and preventing crystallization of amorphous Fe/Al to increase P adsorption sites, and can also inhibit P adsorption by competition with adsorption sites.

(4) Effect of sequential thermal and acid activation

The impurity such as natural organic matter in DWTR can reduce its P adsorption sites and capabilities while it is reused as a P adsorbent (Omoike and VanLoon, 1999). Certain pretreatment procedures are thus necessary to make DWTR into better P immobilizers. The fact that the P adsorption capability can be improved by means of thermal or acid activation on the adsorbent has been widely reported (Karaca et al., 2006; Li et al., 2006; Gan et al., 2009). But, there is no report for improving the adsorption capacity of DWTR through activation. A sequential thermal and acid activation method was used to improve P adsorption capability on DWTR. The optimal conditions were determined as thermal activation at 600℃ for 4 h followed by hydrochloric acid activation at 2 mol/L with a 1:1 solid to liquid ratio. The structure of the DWTR after activation was similar to that before activation; however, the pore volume and surface area were reduced due to the loss of activated carbon during heating. The amount of heavy metal extraction from the activated DWTR partially increased but was below the standards for hazardous waste identification. After activation, the P-binding ability of the DWTR was enhanced, and the maximum P adsorption capacity increased from 28.37 to 53.23 mg g^{-1} (pH = 7), as indicated by the Two-site Langmuir model. The activated DWTR maintained a high P adsorption capability under different redox conditions; even in anaerobic conditions for 64 d. Low pH was beneficial to P adsorption. Fractionation of the absorbed P from the DWTR demonstrated that the activation method was particularly efficient for alum-rich water treatment residuals rather than for ferric-rich water treatment residuals.

2.2 Organophosphorus pesticide, heavy metal, and hydrogen sulfide adsorption by DWTR

(1) Organophosphorus pesticide adsorption by DWTR

Chlorpyrifos and glyphosate as organophosphate pesticides are widely used for both agricultural and domestic pest control worldwide (Eaton et al., 2008). Their use has led to the detection of chlorpyrifos and glyphosate residues in the aquatic environment (Delgado-Moreno et al., 2011; Bhattacharjee et al., 2012; Zhang et al., 2012). DWTR can effectively adsorb chlorpyrifos and glyphosate. The kinetics and isothermal processes of chlorpyrifos sorption to DWTR were better described by a pseudo-second-order model and by the Freundlich equation, respectively. Moreover, compared with paddy soil and other documented absorbents, the DWTR exhibited a greater affinity for chlorpyrifos (log K_{oc}=4.76-4.90) and a higher chlorpyrifos sorption capacity (K_F=5967 $mg^{1-n}\cdot L\cdot kg^{-1}$) owing to the character and high content of organic matter. Further investigation demonstrated that the pH had a slight but statistically insignificant effect on chlorpyrifos sorption to DWTR; solution ionic strength and the presence of low molecule weight organic acids both resulted in concentration-dependent inhibition effects. Meawhile, DWTR exhibited high sorption ability (Q_{max} = 37.9 mg g^{-1}) and stability for glyphosate, of which the sorption capacity was twice higher than that of the reported dewatered alum sludge. These results confirmed the feasibility of using DWTR as a novel adsorbent for chlorpyrifos and glyphosate.

(2) Heavy metals adsorption by DWTR

The characteristics of single metal (Cd and Co) adsorption by DWTR were determined. The adsorption of Cd and Co is a spontaneous endothermic process. The sorption process followed pseudo-second-order kinetics

($R^2=0.99$) and the equilibrium time for Cd and Co sorption were 24 h and 30 h, respectively. The maximum adsorption capacities of Cd and Co were respectively 35.39 mg/g and 17.31 mg/g by using the Langmuir isotherm model ($R^2=0.99$). Fractionation and extraction tests revealed that the adsorbed Cd existed mainly in acid-soluble and residual forms and Co did in acid-soluble form. The FTIR results indicated that Cd and Co interacted with the DWTR surface through strong covalent bond formation as Fe(Al)-O functional groups.

(3) Hydrogen sulfide adsorption by DWTR

The characteristics and mechanisms of hydrogen sulfide adsorption by DWTR in solution were investigated. Results indicate that DWTR had a high hydrogen sulfide adsorption capacity. pH 7 rather than higher pH (e.g. pH 8–10) was favorable for hydrogen sulfide removal. The Yan model fitted the breakthrough curves better than the Thomas model under varied pH values and concentrations. The Brunauer–Emmett–Teller surface area and the total pore volume of the DWTR decreased after the adsorption of hydrogen sulfide. In particular, the volume of pores with a radius of 3–5 nm decreased, while the volume of pores with a radius of 2 nm increased. Therefore, it was inferred that new adsorption sites were generated during the adsorption process. The pH of the DWTR increased greatly after adsorption. Moreover, differential scanning calorimetry analysis indicated that elemental sulfur was present in the DWTR, while the derivative thermal gravimetry curves indicated the presence of sulfuric acid and sulfurous acid. These results indicated that both oxidization and ligand exchange contribute to the removal of hydrogen sulfide by DWTR. Under anaerobic conditions, the maximum amount of hydrogen sulfide released was approximately 0.026 mg g^{-1}, which was less than 0.19% of the total amount adsorbed by the DWTR. The hydrogen sulfide that was released may be re-adsorbed by the DWTR and transformed into more stable mineral forms. Therefore, DWTR are an excellent adsorbent for hydrogen sulfide.

3 Application of DWTR in environmental remediation

3.1 As a substrate in constructed wetlands

Traditionally, constructed wetlands has a limited capacity for the removal of P (Vymazal, 2007). DWTR exhibits a high P adsorption capacity. Thus, it can be used as a potential substrate for enhancing P removal. Reusing DWTR as a substrate in constructed wetlands to treat secondary effluent at short hydraulic retention times (HRTs) (1–3 d) was investigated. Results indicate both continuous flow operation (CFCW) and tidal flow operation (TFCW) can achieve satisfactory removal of total nitrogen (TN), total phosphorus (TP), chemical oxygen demand and suspended solids although the ammonia nitrogen concentration of the CFCW effluent increased slightly. The DWTR was found to be beneficial for denitrification, and the mean nitrate removal rates of CFCW and TFCW were 3.45 and 2.47 g N/m^3d, respectively. The TP removal efficiency of the two DWTR-CWs still remained at 98% after 260 d of operation, and the lifetime regarding P saturation was estimated to be longer than 10 years. The HRT played a more significant role in TN removal, and the most optimal and stable TN removal (>76%) was obtained at 3 d HRT. Moreover, the leaching of Fe and Al from the two DWTR-CWs was minor. Based on regulations, it is feasible to reuse the DWTR as a substrate in constructed wetlands for the purpose of sewage tertiary treatment and waste recycling. In addition, treatment of livestock wastewater was conducted in a two stage constructed wetland system: an intermittent aeration constructed wetland (IACW) and a vertical flow constructed wetlands (VFCW). Results indicate that the constructed wetland system using the DWTR as substrates could effectively remove contaminant (COD, SS, TN, TP, NH_3-N). 58.7 and 60.4% of COD were removed by IACW and VFCW, respectively. And average SS, TN, TP, and NH_3-N removal efficiency reached above 85%.

3.2 As a promising amendment for soil pollution control

(1) Glyphosate pollution control

The feasibility of reusing DWTR as a soil amendment to enhance the retention capacity of glyphosate in two agricultural soils was investigated. Results of batch experiments show that the DWTR amendment significantly enhanced the glyphosate sorption capacity of both soils ($p < 0.001$). Up to 30% of the previously adsorbed glyphosate desorbed from the non-amended soils, and the DWTR amendment effectively decreased the proportion of glyphosate desorbed. Fractionation analyses further demonstrated that glyphosate adsorbed to non-amended soils was primarily retained in the readily labile fraction ($NaHCO_3$-glyphosate). The DWTR amendment significantly increased the relative proportion of the moderately labile fraction (HCl-glyphosate) and concomitantly reduced that of the $NaHCO_3$-glyphosate, hence reducing the potential for the release of soil-adsorbed glyphosate into the aqueous phase. Furthermore, DWTR amendment minimized the inhibitory effect of increasing solution pH on glyphosate sorption by soils and mitigated the effects of increasing solution ionic strength. The present results indicate that DWTR is suitable for use as a soil amendment to prevent glyphosate pollution of aquatic ecosystems by enhancing the glyphosate retention capacity in soils.

(2) Chlorpyrifos and its major metabolite TCP (3,5,6-trichloro-2-pyridinol) control

Amendment of two representative agricultural soils from China with DWTR (0–10 %, w/w) effectively enhanced sorption capacities of both soils for chlorpyrifos and TCP and reduced the rates of chlorpyrifos and TCP desorption from both the soils. The DWTR amendment of the selected soils significantly reduced the bioavailability of chlorpyrifos and both chlorpyrifos and TCP were present in relatively more stable forms in the DWTR-amended soils (5 %, *w/w*) compared with the unamended soils, thus minimizing the ecological risk due to chlorpyrifos and TCP leaching from soils. The detrimental effect of chlorpyrifos and TCP on the soil bacterial communities was attenuated by DWTR amendment, likely due to the decreased bioavailability of chlorpyrifos as a result of DWTR addition. The DWTR amendment resulted in a significantly increased bacterial abundance of one soil but had an insignificant effect on the bacterial abundance of the other soil. Overall, DWTR have high potential to be reused as soil amendments for chlorpyrifos and TCP pollution control.

(3) Multiple metals control

The remediation of soils contaminated with multiple metals using DWTR in Baiyin, China, was investigated. Results of metals fractionation indicate that after the soil was treated with DWTR, arsenic (As), lead (Pb), nickel (Ni), zinc (Zn) and copper (Cu) could be transformed into more stable forms, i.e., As bound in crystalline Fe/Al oxides and other metals in the oxidable and residual forms. However, the forms of chromium (Cr) and cadmium (Cd) were unaffected. Interestingly, due to the effect of DWTR, barium (Ba) was predominantly transformed into more mobile forms. The bioaccessibility extraction test demonstrated that the DWTR reduced the bioaccessibility of As by 25%, followed by Cu, Cr, Zn, Ni, and Pb. The bioaccessibility of Cd and Ba were increased; in particular, there was an increase of 41% for Ba at the end of the test. DWTR can be used to remedy soil contaminated with multiple metals, but comprehensive studies are needed before practical applications of this work.

3.3 Phosphorus immobilization in lake sediments

(1) Effect of DWTR on the activities of inorganic P and organic P in the sediments

The sediments were sampled from Baiyangdian Lake (Lake B) and Taihu Lake (Lake T). DWTR was thoroughly mixed with sediments. After cultivation, samples were taken to analysis. Results indicate that DWTR was able to reduce the inorg-P activity in sediment by transforming BD-P to NaOH-P. Although the sediments in Lake T and Lake B had dissimilar properties, DWTR was found to reduce the inorg-P activity in both sediments within 10 days after a 10% application of DWTR (dry weight) to the sediment samples. On the other hand, DWTR was found to have little effect on the activity of org-P. Inorg-P released from sediments into lake water can cause eutrophication. Therefore, DWTR could be used to control eutrophication in lakes by way of their ability to immobilize inorg-P in lake sediment.

(2) Effect of light, microbial activity, and sediment resuspension

Laboratory scale experiments were conducted to investigate the effects of light, microbial activity, and sediment resuspension on the P immobilization capability of DWTR. Results suggest that absence of light, low microbial activity, and sediment resuspension can increase the internal P loading from lake sediments. DWTR can, however, reduce the internal P loading significantly. Further analysis demonstrated that DWTR can stabilize P, decreasing the P bioavailability in the sediments under varied conditions. DWTR also presented little undesirable effects on the dissolved oxygen levels and pH of overlying water. Therefore, light, microbial activity, and sediment resuspension have little effect on the P immobilization capability of DWTR in lake sediments.

(3) Effect of H_2S

The lability of P in sediments varies with numerous environmental factors, e.g., temperature, dissolved oxygen and H_2S contents (Smith and Klug, 1981; Jiang et al., 2008). Among them, H_2S content has a significant effect on the lability of P in sediments. In lakes, H_2S can be formed by the reduction of sulfate under anaerobic conditions (Smith and Klug, 1981). Sulfate reduction is less significant under oligotrophic conditions but has significant potential in eutrophic lakes (Marianne and Storkholm, 2001). In lake sediments, H_2S can compete with P for adsorption sites, causing the internal P loading to become more serious (Nürnberg, 1984). The lability of P in DWTR amended sediments may vary with hydrogen sulfide content. Thus, the effect of H_2S on the lability of P in DWTR amended sediments need to be investigated. Results indicate that H_2S can significantly increase the lability of P in raw sediments. However, after the sediments were amended with DWTR, H_2S had only minor effects on the lability of P. The amended sediments also had higher H_2S adsorption capability than the raw sediments. In the presence of H_2S, Loose-P, Al-P, Fe-P, O-P and Ca-P were desorbed from the raw sediments, whereas only Loose-P and O-P were desorbed from the amended sediments. Moreover, the desorbed P was transformed into Al-P and Fe-P in the amended sediments. Therefore, the lability of P in the DWTR amended sediments was not increased by H_2S.

(4) Effects of settling

In the envisioned practical application, DWTR would be added to the lake, would settle to the lakebed and then would reduce the internal P loading. During settling, physical, chemical and microbial reactions may result from the interaction of DWTR with other substances in lake water, which may affect the P immobilization capability of DWTR (Boyer et al., 2011). Therefore, it is essential to understand differences in the P immobilization capabilities of DWTR before and after settling from lake water. Both batch and incubation experiments were conducted to assess the P immobilization capabilities of DWTR before and after settling from lake water. Results demonstrate that DWTR have a low risk of leaching metals during settling. The DWTR had a lower P adsorption rate after settling, but their P adsorption capacities differed little under different P concentrations and pH. Moreover, the DWTR had similar capabilities to immobilize P in lake sediments before and after settling. Altogether, these results indicate that the P immobilization capability of DWTR changes little after DWTR settle from lake water. Thus, the use of DWTR to immobilize P in sediments may be a feasible, practical technique for lake restoration.

(5) Effect of DWTR dosage

Prior to widespread application of Al/Fe based DWTR, it is necessary to determine the required dosage of the DWTR for effective sediment P immobilization. Previous studies have shown that the P sorption capacity of

Al/Fe based DWTR is closely related to their oxalate-extractable Al and Fe (Al_{ox} and Fe_{ox}) content (Dayton and Basta, 2005). Therefore, it may be possible to determine the required dosage of Al/Fe based DWTR for P immobilization in enriched sediments based upon the Fe_{ox} and Al_{ox} content of the DWTR used and the quantity of mobile P (P_m) in the sediments. An equation ((Al_{ox} + Fe_{ox})DWTR = 83*P_m–40 (where Al_{ox}, Fe_{ox} and P_m are expressed in μmol g^{-1}),) was established to calculate the dosage for DWTR to immobilize P in lake sediment. This equation was successfully used to determine the respective quantities of three different Al/Fe based DWTR required to immobilize P in sediments from Lake Chaohu, Lake Taihu, the Changjiang River, the Haihe River, the Pear River and the Yellow River. Using the equation derived herein, the required Al/Fe based DWTR application dose can easily be determined where the P_m content of the sediment and the Al_{ox} and Fe_{ox} content of the DWTR are known.

(6) Effects of DWTR aging

As an Al/Fe based agent, the aging process may be one of the most important factors affecting its P adsorption capability. It has been reported that Al salts in lake water tend to be crystallized (Berkowitz et al., 2005), and with this process, the P adsorption capability of Al decreases (Berkowitz et al., 2006). Even the maximum adsorption capacity was found to decrease by 75% of total after 90-day aging (de Vicente et al., 2008). Therefore, determination of the aging effect on the stability of internal P pollution control by DWTRs is essential. Based on a 180-day incubation test, the aging effect of DWTRs under different pH and redox conditions was investigated. Result show that the DWTRs before and after incubation under different conditions have similar structures, but their specific surface area and pore volume, especially mesopores with radius at 2.1-5.0 nm drastically decreased. The oxalate extractable Al contents changed little although a small amount of Al transformed from oxidizable to residual forms. The oxalate extractable Fe contents also decreased by a small amount, but the transformation from oxidizable to residual forms were remarkable, approximately by 14.6%. However, the DWTR before and after incubation had similar P immobilization capabilities in solutions and lake sediments. Even the maximum P adsorption capacity estimated by the Langmuir model increased after incubation. Therefore, it was not necessary to give special attention to the impact of Al and Fe aging on the effectiveness of DWTRs for geoengineering in lakes.

(7) The stability of P in the DWTR amended sediments

A chemical treatment that uses active materials to increase the stability of P in sediments was considered an effective method for combating P loading (Egemose et al., 2010). The reuse of DWTR as active materials in the chemical method for lake restoration is beneficial from both environmental and economic standpoints. However, one potential concern related to the use of DWTR is that the P loading from sediments can be affected by many factors (Jiang et al., 2008). Therefore, the stability of P in lake sediments amended with DWTR under various conditions need to be assessed. Results suggest that DWTR could make P more stable in each of the lake's sediments. DWTR can significantly decrease the P desorption potential under the range of pH in the natural environment (5-9) and reduce the competitive effects of SiO_4^{2-} on P. Organic matter in sediments, ion strength and anaerobic condition also did not affect the stability of P in the DWTR-amended sediments. Moreover, DWTR can increase the P adsorption rate and capacity of the sediments. Overall, application of DWTR to control the internal P loading for lake restoration is feasible.

4 The potential toxicity of DWTR application

4.1 Heavy metal risk

(1) Metals extractability from DWTR

Prior to practical application, it is essential to assess the potential environmental risks posed by DWTR use, including the evaluation of the potential for metal contamination (Smith, 2009). Due to the high quality of raw water in drinking water treatment plants, heavy metals in DWTR are typically present at low levels (Elliott et al., 1990; Elliott and Taylor, 2000), and DWTR are often considered non-hazardous (Makris et al., 2005). At present, there is a dearth of information concerning the lability of metals in DWTR. The extractability of Al, Fe, As, Ag, Ba, Be, Ca, Cd, Co, Cr, Cu, Hg, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sr, V, and Zn in six DWTR collected throughout China was investigated using fractionation, in vitro digestion, and the toxicity characteristic leaching procedure (TCLP). Moreover, the potential risk of metal pollution due to environmental use of the selected DWTR was assessed. Results show that the DWTR investigated were relatively enriched in Al, Fe, Ca, and Mg, particularly Al and Fe, and also contained lesser concentrations of As, Ba, Be, Cd, Co, Cr, Cu, K,Mo, Mn, Na, Ni, Pb, Sr, V, and Zn, but no Ag, Hg, Sb, or Se. Most of the metals within the DWTR were largely non-extractable by the BCR procedure, but many metals exhibited high bioaccessibility based on in vitro digestion. However, the DWTR could be considered non-hazardous based on the TCLP assessment method used by the USEPA. Overall, the metal concentrations and extractabilities from different DWTR often vary, and recycling of DWTR should be based on assessment using relevant regulatory guidelines and results of chemical analyses.

(2) Metal lability in air-dried and fresh DWTR

The metal pollution risk could be closely related to the metals lability, which often varies with the changes in actual environmental conditions and pre-treatment of DWTR (Agyin-Birikorang and O'Connor, 2009). For pretreatment, most laboratory studies used the air drying method (Makris et al., 2006b; Zhou and Haynes, 2011); however, in field studies, fresh dewatered samples were often applied directly (Agyin-Birikorang et al., 2009; Zhao et al., 2011b). To ensure the safe reuse of DWTR, it is very important to determine the effect of air-drying on the metals’ lability in DWTR. Therefore, in this work, the labilities of Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Sr, V, and Zn in air-dried and fresh dewatered DWTR were monitored and compared using the Toxicity Characteristic Leaching Procedure (TCLP), fractionation, in vitro digestion and a plant enrichment test. The results showed that the air-dried and fresh dewatered DWTR had different properties, e.g., organic matter composition and available nutrients. The air-dried and fresh dewatered DWTR were non-hazardous according to the TCLP assessment method used in the United States; however, the metals in the two types of DWTR had different lability. Compared with the metals in the fresh dewatered DWTR, those in the air-dried DWTR tended to be in more stable fractions and also exhibited lower bioaccessibility and bioavailability. Therefore, air-drying can decrease the metal lability and thereby reduce the potential metal pollution risk of DWTR.

(3) Effect of pH

Some researchers have considered that metal lability (e.g., Mn) in DWTR may change with pH (Novak et al., 2007; Lombi et al., 2010). These results suggest that a comprehensive understanding of the lability of metals in DWTR is very important. The lability of metals often varies with environmental conditions (Zeng et al., 2011), among which pH was considered an important factor (Eggleton and Thomas, 2004). Therefore, it is important to determine the effect of pH on metal lability in DWTR. Batch tests and then fractionation, in vitro digestion, and the toxicity characteristic leaching procedure were used to investigate the release and extractability of metals in DWTR under different pHs. Results demonstrate that significant release from DWTR for Ba, Be, Ca, Cd, Co, Cr, Fe, Mg, Mn, Pb, Sr, and Zn occurred under low pH (acid condition); for As, Mo, and V under high pH (alkaline condition); and for Al, Cu, and Ni under both conditions. In comparison, most metals in the DWTR were more easily released under low pH, but the release was stable at a relatively low level between pH 6 and 9, especially under alkaline conditions. Further analysis indicated that the chemical extractability and bioaccessibility of many metals was found to increase in the DWTR after being leached, even though the leached DWTR could still be considered nonhazardous. These results demonstrated that pH had a substantial effect on the lability of metals in DWTR. Overall, caution should be used when considering pH conditions during DWTR reuse to avoid potential metal pollution.

(4) Effect of anaerobic incubation of DWTR

The pH and redox conditions were the two main factors affecting the lability of inorganic contaminants in the environment (Eggleton and Thomas, 2004). As indicated by above section, the lowest potential for metal release from DWTR was at pH 6–9, which was also recommended as the optimal pH for DWTR reuse. To date, there is little information on the effects of redox status on the lability of metals in DWTR. In the envisioned practical application (e.g., soil, water and sediment), the most common conditions for the application of DWTR involve an anaerobic or anoxic environment. Under these conditions, the lability of metals in solid materials (e.g., soils (Frohne et al., 2011) and municipal solid waste (Prechthai et al., 2008)) may change. Therefore, based on an anaerobic incubation test, the lability of metals in DWTR was investigated using fractionation, in vitro digestion and the toxicity characteristic leaching procedure (TCLP). Results indicate that most metals in the DWTR were stable during anaerobic incubation and that the DWTR before and after incubation could be considered non-hazardous in terms of leachable metal contents according to US EPA Method 1311. However, the lability of certain metals in the DWTR after incubation increased substantially, especially Mn, which may be due to the reduction effect. Therefore, although there is no evidence presented to restrict the use of DWTR in the field, the lability of metals (especially Mn) in DWTR requires further assessment prior to field application. In addition, fractionation (e.g., BCR) is recommended for use to determine the potential lability of metals under various conditions.

4.2 Ecological risk assessment of DWTR

(1) The toxicity of DWTR to *Chlorella vulgaris*

Chemical analysis indicated that DWTR can be considered to be non-hazardous according to the toxicity characteristic leaching procedure assessment method used by the United States Environmental Protection Agency. In order to comprehensively evaluated the potential ecotoxicity of DWTR. The effect of DWTR on organisms including bioavailability, potential synergistic effect, or toxicity needs to be investigated. Alga is one of the model organisms for ecotoxicity tests, and has been widely used for ecotoxic risk assessment of waste (Elliott and Taylor, 2000). Alga does not only produce biomass that forms the basic nourishment for food webs but also contribute to the self-purification of polluted water (Long et al., 2012). Accordingly, the ecotoxicity of dewatered DWTR leachates to a green alga, *Chlorella vulgaris* (*C. vulgaris*) was evaluated. Results indicate the potential effect of DWTR leachates on algal growth included both growth inhibition and promotion. The inhibition effect was resulted from P deficiency of leachates caused by the adsorption of P by DWTR. The metals and NH_4-N released by DWTR in leachates promoted algal growth. Further analysis showed that oxidative stress and photosynthesis inhibition induced by exposure to DWTR leachates were readily mitigated within a short time. Therefore, the environment recycling of dewatered, air-dried DWTR does not represent an ecotoxicological risk to green algae, but may lead to environmental P deficiency.

(2) Bacterial toxicity assessment of DWTR

The toxicity of DWTR and sediments amended with DWTR to *Aliivibrio fischeri* was evaluated based on the Microtox® solid and leachate phase assays, in combination with flow cytometry analyses and the kinetic luminescent bacteria test. Results show that both solid particles and aqueous/organic extracts of DWTR exhibited no toxicity to the bacterial luminescence and growth. The solid particles of DWTR even promoted bacterial luminescence, possibly because DWTR particles could act as a microbial carrier and provide nutrients for bacteria growth. Bacterial toxicity (either luminescence or growth) was observed from the solid phase and aqueous/organic extracts of sediments with or without DWTR addition. Further analysis showed that the solid phase toxicity was determined to be related mainly to the fixation of bacteria to fine particles and/or organic matter, and all of the observed inhibition resulting from aqueous/organic extracts was identified as non-significant. Moreover, DWTR addition not only had no adverse effect on the aqueous/organic extract toxicity of the sediment but also reduced the solid phase toxicity of the sediment. Overall, in practical application, the solid particles, the water-soluble substances transferred to surface water or the organic substances in DWTR had no toxicity or any delayed effect on bacteria in lakes, and DWTR can therefore be considered as a non-hazardous material.

(3) Effect of DWTR on the survival of microorganism in lake sediment

Application of DWTR could cause the change of total bacteria structure in lake sediment, and also could increase the abundance of total bacteria, but had little effect on total bacterial diversities. Further studies showed that DWTR addition were beneficial to anaerobic ammonium oxidation (anammox) bacteria aggregation in sediment, causing the activity of anammox bacteria to increase from 6.1 nmol-N g^{-1} h^{-1} to 9.2 nmol-N g^{-1} h^{-1} and the abundance to increase from 8.9×10^7 copies g^{-1} to 9.8×10^7copies g^{-1}, and also increased the diversity of anammox bacteria in sediment, leading to anammox phylogenetically being more closely related to *Candidatus* Brocadia. DWTR addition could slightly increase the nitrification potential of lake sediment, which were from 12.8 μg-N g^{-1}-(dry sample) h^{-1} to 13.2 μg-N g^{-1}-(dry sample) h^{-1}, and increase the abundances of ammonia oxidizing bacteria (AOB) and nitrite oxidizing bacteria (NOB) in sediment from 1.1×10^8 (AOB) and 8.6×10^4 (NOB) copies g^{-1}dry sample to 1.3×10^8 and 9.4×10^4 copies g^{-1} dry sample, respectively. DWTR addition was also beneficial to the enrichment of *Nitrosomonas* and *Nitrosospira multiformis* and promoted the emergence of a new *Nitrospira* cluster, causing the increase in AOB and NOB diversities. However, DWTR had minor effects on the morphologies of AOB and NOB in sediments.

5 Future perspectives of applying DWTR

Overall, DWTR is an effective adsorbent of many contaminants, and can be recycled in environmental remediation. Our previous works investigated the adsorption characteristics and the potential ways for DWTR recycling in environmental remediation comprehensively. However, the work on recycling DWTR in environmental remediation has been completed in lab tests, which cannot guarantee similar effects in complex environment. With this regard, the filed-scale studies are ongoing (Fig. 1), particularly the contaminants (P, heavy metals, organic pollutants) immobilizing performance and potential toxicity of DWTR being evaluated. Moreover, as indicated by previous study, a specific characteristic of P adsorption by DWTR is a long-term equilibrium and the processes can be maintained for >80 d (Makris et al., 2005). Generally, P often release slowly from sediment into water column, but, the traditional inactivating materials commonly show a good P immobilizing performance in a short time. In lake remediation, traditional inactivating materials are thus recommended for application in single large doses or in repeated doses to obtain desirable restoration effects. Single large doses increased the potentially unfavorable effect on the surroundings (Gołdyn et al., 2014) and inactivating materials dosed in repetition increased the cost of lake remediation. Therefore, in consideration of DWTR P adsorption characteristics and traditional inactivating materials properties, a new type DWTR is being explored. The modification technology and combined with other traditional inactivating materials are being adopted to obtain an ideal P remediation materials. In addition, DWTR is commonly reused in powder form, which may accelerate filtration system clogging due to lower hydraulic conductivity. Generally, a media size of 5-20 mm is used in filtration systems such as constructed wetlands. To satisfy industrial use demand, powdered

DWTR must be transformed into a granular form with high mechanical strength. Efforts are needed to develop granular DWTR, and the attempts to granulate DWTR have already been carried out (Fig. 2). The preliminary performance evaluation showed that the granular DWTR exhibited strong P adsorption capability and good mechanical stability.

Fig. 1 Future field-scale experimental site.

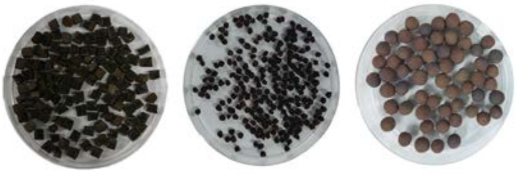

Fig. 2 Three kinds of granular DWTR

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