A comparison of the phosphorus immobilization capabilities of water treatment residuals before and after settling from lake water

Changhui Wang, Yuansheng Pei *

The Key Laboratory of Water and Sediment Sciences, Ministry of Education, School of Environment, Beijing Normal University, Beijing 100875, PR China

ABSTRACT

Drinking water treatment residuals (WTRs), which are by-products generated during drinking water treatment processes, could be used to immobilize phosphorus (P) in lake sediments, thereby allowing for control of the internal P loading of a lake. Prior to applying WTRs for this purpose on a large scale, it is necessary to determine the P immobilization capabilities of WTRs under various conditions. This work investigated the P immobilization capabilities of WTRs before and after settling from lake water. The results demonstrated that WTRs have a low risk of leaching metals during settling. The WTRs had a lower P adsorption rate after settling, but their P adsorption capacities differed little under different P concentrations and pH. Moreover, the WTRs had similar capabilities to immobilize P in lake sediments before and after settling. Altogether, these results indicate that the P immobilization capability of WTRs changes little after WTRs settle from lake water. Thus, the use of WTRs to immobilize P in sediments may be a feasible, practical technique for lake restoration.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Drinking water treatment residuals (WTRs) are by-products generated in water treatment plants [1,2]. They are primarily composed of amorphous Fe/Al hydroxides because Fe/Al coagulants are often used to purify raw water [3]. Studies have demonstrated that the amorphous structures of Fe and Al in WTRs endow these residuals with high adsorption capability for many contaminants, such as phosphorus (P) [4,5], metals [6,7], perchloric acid [8] and hydrogen sulfide [9]. Among these contaminants, the adsorption of P to WTRs is of particular interest to investigators [2]. WTRs have high, stable P adsorption capability [10–12], and, once adsorbed, P desorption is difficult [13]. WTRs have been used as soil additives to control off-site P pollution [14] and as a primary medium in constructed wetlands to remove excessive P from wastewater [15,16]. These studies are important demonstrations of the ability to recycle WTRs. However, currently, WTRs are primarily disposed of in landfills despite the fact that this method is costly and consumes

land resources [1]. Therefore, investigating new ways of recycling of WTRs is still a topic of current research.

More recently, researchers found that WTRs can remove excessive P in lake water [17] and can immobilize P in lake sediments [18], suggesting that the application of WTRs may be an ideal method of reducing the internal P loading in lake to control eutrophication. The internal P loading has been considered to be one of the main reasons for excessive P in lake water [19–21]. Developing a method to recycle WTRs to reduce internal P loading would thus be a "win–win" technique for lake restoration.

Prior to utilizing WTRs in restorative efforts, it is necessary to investigate their P immobilization capabilities under various conditions. One question concerns the P immobilization capability of WTRs after they have settled from lake water. In the envisioned practical application, WTRs 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 WTRs with other substances in lake water, which may affect the P immobilization capability of WTRs [17]. Therefore, it is essential to understand differences in the P immobilization capabilities of WTRs before and after settling from lake water.

In this work, both batch and incubation experiments were conducted to assess the P immobilization capabilities of WTRs before and after settling from lake water. The results of this study provide theoretical supports for utilizing recycled WTRs to immobilize P in sediments in lakes for restorative purposes.

2. Materials and method

2.1. Sample collection

Raw WTRs were collected from the Beijing City No. 9 Waterworks in China. The WTRs were dried in air, ground and filtered through a sieve with a particle diameter of less than 1 mm. The WTRs had a surface area of 78.83 $m^2 g^{-1}$ and contained 0.61 $mg g^{-1}$ P, 57.65 $mg g^{-1}$ organic matter, 101.56 $mg g^{-1}$ Fe and 50.36 $mg g^{-1}$ Al [22,23]. The results of XRD and SEM analyses suggested that the Fe and Al in WTRs were poorly crystalline [23]. Detailed characteristics of WTRs are given in Wang et al. [23]. The lake sediment samples were obtained from Lake Baiyangdian (38°53′N, 115°59′E) in the Zhainan village in September 2011. The samples were collected from the uppermost 10 cm of the lake sediment using a Petersen grab sampler, filtered through a 1.8 mm screen to remove impurities, mechanically homogenized and stored in acid-cleaned polyethylene flasks at 4 °C. The characteristics of these sediments were reported previously by Wang et al. [18]. Lake water was sampled at the same location at a depth of approximately 1.5 m. The dissolved oxygen level of the lake water was 3.2 $mg L^{-1}$, the turbidity was 8.1 NTU and the water temperature was 17 °C. The lake water was filtered through 0.45 μm Millipore filter paper and stored at 4 °C.

2.2. Sample preparation and analysis

To examine the differences in the P immobilization capabilities of WTRs before and after settling from lake water, P-rich lake water was prepared by adding P (KH_2PO_4) to raw lake water to a final P concentration of 1 $mg L^{-1}$. Therefore, two types of lake water were used in this study: raw lake water and P-rich lake water.

The settleability of the raw WTRs in lake water was investigated. Briefly, 100 mL of raw or P-rich lake water was added to a 100 mL measuring cylinder placed on an experiment table. One gram of raw WTRs was added slowly to the measuring cylinder, and the uppermost layer of lake water (80 mL) was sampled at 0.08, 0.17, 0.25, 0.50, 1.00, 1.50, 2.00 and 4.00 h. The sample solutions were filtered on oven-dried, 0.45 μm Millipore filter paper. The papers were oven dried again after filtering. The difference in mass in the oven-dried Millipore filter paper before and after filtering was used to calculate the contents of WTRs remaining in the lake water layer (80 mL). In addition, turbidity measurement was also done at the end of the experiment.

During settling, physical, chemical and microbial reactions may result from the interaction of WTRs with other substances in lake water. To obtain WTRs that had settled from lake water, a simulation experiment was conducted to simulate these interactions. The raw WTRs were mixed with either raw or P-rich lake water at a ratio of 1:100 (solid:solution, g mL^{-1}) in conical flasks, and then the mixtures were shaken for 24 h at 25 °C and centrifuged to separate the solid and liquid components. The solids were freeze dried, ground and mixed; the liquids were filtered through 0.45 μm Millipore filter paper and stored at 4 °C. This approach yielded two different WTRs samples for this study: settled WTRs from raw lake water and settled WTRs from P-rich lake water.

The total concentrations of Ag, As, Cd, Cr, Hg, Ni, Pb, Se, Cu, Zn, Al, Fe, Ca, Mg, Mn, P, S and Cl in the raw and P-rich lake waters were determined before and after the simulation experiment using an inductively coupled plasma-atomic emission spectrometer (ICP-AES, ULTIMA, JY, France). The total organic carbon (TOC) in the lake water was measured using a TOC analyzer (LiquiTOC, Elementar), and the pH of the lake water was measured using a pH meter (pH-10, Sartorius). The pHs of the raw and settled WTRs were determined by measuring the supernatant of a 1:2.5 solid:solution (g mL^{-1}) suspension. The contents of oxalate-extractable Fe (Fe_{OX}) and Al (Al_{OX}) in the raw and settled WTRs were also determined. Fe_{OX} and Al_{OX} in the WTRs were extracted using oxalates solutions (pH 3) at a ratio of 1:60 (solid:solution, g mL^{-1}) following the procedure described by Makris et al. [4], and the Fe_{OX} and Al_{OX} contents were measured using ICP-AES.

2.3. Batch experiment

The P adsorption kinetics of the raw and settled WTRs were studied. A series of mixtures containing WTRs samples (0.3 g) and solutions (30 mL, pH 7) of 10 mg P L^{-1} in 0.01 M KCl were prepared. The mixtures were shaken at 25 °C for 2, 4, 6, 8, 10, 12, 24 or 48 h, after which the P concentrations were determined. Measurements were prepared in triplicate, and the data are expressed as the mean values. The standard error for each measurement was below 10%.

From the results of the kinetics study, the P adsorption equilibrium time was determined and was used to investigate the P adsorption capabilities of the raw and settled WTRs at different P concentrations and pHs. For the former experiment, WTRs samples (0.3 g) were mixed with a series of 30 mL solutions containing 0.01 M KCl at pH 7 and variable concentrations of P (2, 4, 6, 8, 10, 12, 16 or 32 mg L^{-1}). The mixtures were shaken at 25 °C until reaching equilibrium, at which point the P concentration of each solution was determined. The effect of pH was determined in an analogous experiment using solutions supplemented with 10 mg L^{-1} P at a pH of 5, 7 or 9.

2.4. Incubation experiment

The raw and settled WTRs were mixed with the raw lake sediments to a dry weight proportion of approximately 10% WTRs, and then the mixtures were incubated at 15 °C for 10 days. The results of a previous study indicated that the raw WTRs can immobilize most of the mobile P in lake sediments under these conditions [18]. After completion of the incubation experiments, the mixtures were freeze dried, ground and filtered through a standard 100-mesh sieve for further testing. A control reaction was run in conjunction with the incubation experiment.

Fractionation was used to analyze the various forms of P present in the sediment samples before and after the incubation experiment. Sediment samples (1 g) were extracted sequentially with 25 mL 1 M NH_4Cl for 4 h (NH_4Cl-P), 25 mL 0.11 M $Na_2S_2O_4$/ 0.11 M $NaHCO_3$ for 2 h (BD-P), 25 mL 1 M NaOH for 16 h (NaOH-P) and 25 mL 0.5 M HCl for another 16 h (HCl-P) [24]. Solutions obtained from the second extraction step were stored overnight at 4 °C prior to P analysis to oxidize the residual extraction reagent [25]. Experiments were performed in triplicate, and the data are expressed as the mean. The standard error in the measurements was within 10%.

3. Results and discussion

3.1. Characterizations of the lake water and WTRs

The settleabilities of the WTRs in raw lake water and P-rich lake water are shown in Fig. 1. The settleabilities measured for the WTRs in raw and P-rich lake waters were similar. After the first 0.08 h, approximately 0.06 g WTRs remained in both lake water samples. Given the initial addition of 1 g of WTRs, this result suggested that 94% WTRs had settled within that time. After 2 h, the lake water contained no WTRs. By measuring the height (0.14 m) of the water (80 mL) contained in the measuring cylinder, the average settlement velocity of 94% of the WTRs was calculated as