Review

Granulation of Drinking Water Treatment Residues: Recent Advances and Prospects

Baiming Ren ^{1,2,*} , Yaqian Zhao ^{1,*} , Bin Ji ¹, Ting Wei ¹ and Cheng Shen ²

¹ State Key Laboratory of Eco-Hydraulics in Northwest Arid Region, Xi'an University of Technology, Xi'an 710048, China; binjisl@163.com (B.J.); tingwei93@163.com (T.W.)

² Centre for Water Resources Research, School of Civil Engineering, University College Dublin, Belfield, Dublin 4, D04, Ireland; shen.cheng@ucdconnect.ie

* Correspondence: ren.baiming@ucdconnect.ie (B.R.); yaqian.zhao@ucd.ie (Y.Z.)

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Abstract: Beneficial reuse of drinking water treatment plant residues (WTRs) has been intensively studied worldwide in the last decades, but few engineering applications can be found. The majority of WTRs were directly reused in cake form (after dewatering), e.g., alum sludge cake as main substrate used in constructed wetlands (CWs), or oven dried and ground powdery form, e.g., sorbent for pollutant removal. However, WTRs reuse in such forms has several drawbacks, i.e., difficulty of recovering and easy clogging (in CWs), which result in limited WTRs engineering applications. Granulation or pelleting could widen and be a wiser WTRs reuse route and also seems to be a promising strategy to overcome the “application bottleneck” issues. In the literature, a number of trials of WTRs granulation have been reported since 2008, including sintering ceramicsite, gel entrapment and newly emerged techniques. Hence, there is a need to overlook these studies and promote WTRs granulation for further development. To this end, this review firstly provides a piece of updated comprehensive information and critical analysis regarding WTRs granulation/pelleting technology. It aims to enhance WTRs granulation studies in the developing stage and thus enlarge WTRs engineering applications.

Keywords: alum sludge; pelleting; review; sintering; substrates; adsorption

1. Introduction

The booming of population and urbanization has caused a worldwide potable water demand. However, from a technical point of view the production of reliable and safe drinking water is always accompanied by the generation of water treatment residues (WTRs) [1]. Since the conventional water treatment plants (WTPs) involve the processes of coagulation, flocculation, sedimentation, filtration and disinfection, a large quantity of residues as an inevitable by-product were generated during the “flocculation/coagulation” processes known as WTRs [2].

WTR production from drinking water treatment is generally estimated to represent 1%–3% in volume of the raw water used during the treatment process [3]. However, specific data on the global or regional level showed that the WTRs generation are seldom available because the local authorities usually publish the waste statistics in a broad category instead of specifying each waste type, e.g., WTRs were always wrongly associated with wastewater treatment plant sludge (sewerage sludge) [1]. Thus, it is difficult to retrieve the exact WTRs generation of a country or region and only 15 countries' WTRs annual generation data were found in the literature [1,4–6]. As shown in Figure 1, the WTRs generation in China is the largest at 2.3 million tons per year, however, the largest quantity of annual WTRs generation per person was found in South Korea. By contrast, Denmark has the least WTRs generation of 10,000 tons/year as well as the quantity of annual WTRs generation per person among the fifteen

countries. The sludge disposal cost in the Netherlands stands at a huge sum of USD 37–50 million per year, and USD 6.2 million per year in Australia. It was also estimated that the alum sludge disposal cost in Ireland will be doubled by the end of the next decade from the present assessment of 15,000 to 18,000 tons/year of the dried solids [7–10].

Figure 1. Annual water treatment residues (WTRs) generation of 15 countries.

Therefore, WTRs disposal and the associated cost as well as the environmental impacts are still worldwide issues. Historically, the simple and thoughtless disposal routes of WTRs, i.e., discharge to a natural water body, discharge to sewer, discharge to lagoons, waste landfill, engineering fill, bring adverse environmental impacts [1,3]. At present, landfilling has been the most widely applied method in most countries over the world (i.e., China, Ireland, France, etc.) and still has the possibility of contaminating water bodies and soils from the chemical products used in the treatment [11]. From the viewpoint of the “3R principle”: reduce, reuse, and recycle, it is crucial to identify viable management options for WTRs, particularly where WTRs can be effectively utilized in an environmentally acceptable and sustainable manner [12]. It has been proven by a number of studies that WTRs are resources, rather than waste [13–15]. To date, there are four broad categories of WTRs beneficial reuse routes. These efforts include the use in wastewater treatment processes, use as building/construction materials, land-based applications and coagulant recovery and reuse [4]. It is worth noting that majority of WTRs was reused in a powdery form (sorber for pollutants removal), which was through the dried, ground and sieved processes [8]. However, the powdery form WTRs hinders its wide engineering applications and makes it even less attractive as adsorbents since it is difficult to recover powdery WTRs (as sorbents) from the adsorption process [16]. Moreover, there has been a concern that the direct reuse of WTRs cake (after dewatering) as substrates in constructed wetlands (CWs) was likely to cause clogging due to their low hydraulic conductivity [17,18]. Hence, converting raw WTRs into useful value-added products is of great interest worldwide, which can not only alleviate the above-mentioned recovery and clogging issues but also offer wider and wiser WTRs reuse routes.

Granulation, a technique of particle enlargement by agglomeration, is one of the most significant and common unit operations in the production of pellet/granular forms [19]. During the granulation process, small fine or coarse particles of WTRs are converted into large agglomerates [18]. These pellet type WTRs are easy to separate and recover from adsorption process, and are more suitable to be used as a substrate in CWs, due to the increased compressive strength and hydraulic conductivity [20,21]. Therefore, WTRs granulation could be a wiser and more comprehensive WTRs reuse route and seems also to be a promising strategy to overcome the WTRs engineering application bottleneck issues.

Up to now, a number of trials have been carried out worldwide on the reuse of WTRs for granulation of novel value-added products, and the resultant products were used as sorbent or substrates in CWs. However, to the best of our knowledge, there is no comprehensive review regarding WTRs granulation technology. Thus, this review aims to provide an updated guideline for the WTRs granulation technology as well as to identify the promising areas of further research and development. Several keywords including “water treatment residues, waterworks residues, alum sludge, granulation, pelleting, sintering and gel entrapment” were employed on the “Web of Science”, “Scopus” and “Google Scholar” databases. From the year 2000 to 2020, only 14 studies (from over 1800 searched results) were dealing with the presented topic, hence they were comprehensively reviewed and discussed. It is expected that the review could enhance WTRs granulation studies to further develop and enlarge WTRs engineering applications.

2. Recent Advances of WTRs Granulation and Their Applications

The first trial of WTRs granulation was carried out in 2008 [22]. Generally, the total 14 studies can be classified by the various granulation techniques in three broad categories, i.e., sintering WTRs ceramsite, gel entrapment and newly emerged techniques, e.g., freeze–thaw process and natural curing. The details of relevant studies are presented in Table 1 and discussed as follows.

2.1. Sintering WTRs Ceramsite

Xu et al. [22] firstly reported on the mixing of wastewater treatment sludge (55%), alum sludge (45%) and water glass to produce sludge ceramsite. The study aimed to solve the disposal issues of sewerage sludge and waterworks residues, simultaneously. Pellet sludge products (particle sizes of 5–8 mm) were left at room temperature for 3 days and then dried at 110 °C for 24 h. Sample sintering was started at 20 °C and continued at a rate of 8 °C/min to 200 °C, 600 °C, and 800 °C for 10 min and at 1000 °C for 35 min. Finally, the samples were naturally cooled until they reached room temperature. In another study reported by Zou et al. [23], the resultant sludge ceramsites were used as carrier/media in a biofilter aimed to treat chemical oxygen demand (COD) and total nitrogen (TN) in wastewater. Results indicated that the ceramsite-based biofilter could remove 79.1%–86.4% of ammonia nitrogen (NH₄-N) and 43.9%–51.0% of TN. Similarly, Chen et al. [21] also reported an alum sludge ceramsite. It was used as substrate in laboratory-scale CWs for biofilm development and pollutants removal from wastewater. The granulation process was carried out by mixing alum sludge and clay in the ratio of 3:1 and pelletized into balls (6–8 mm). Samples were then dried at 105 °C for 2 h. The pelletized raw material was preheated at 400 °C for 30 min and sintered at 1050 °C for 10 min. Results indicated that the biofilm growth rate was 0.49 mg/(g·day) on the alum sludge ceramsites (5.98 times higher than that of commercial ceramsites). It is likely due to the greater specific surface area. Moreover, 98.6%, 91.0%, and 85.8% of total phosphorus (TP), TN, and COD were removed, respectively. In addition, Wang et al. [24] also investigated a CW substrate made by waterworks sludge ceramsites which contained fly ash and river sediment for wastewater purification. Results suggested that COD, NH₄-N, and TP were stably removed by 70%, 60% and 79%, respectively. However, the detailed methods regarding the WTRs granulation process were not specified.

Bae et al. [25] also reported a pellet-type adsorbent based on alum sludge for the removal of gaseous trimethylamine (TMA). Alum sludge was pretreated with H₃PO₄ solution in a batch reactor at 110 °C for 2 h. The resulting solid was filtered and washed, followed by drying at 60 °C for 24 h and then 110 °C for 12 h. The pretreated alum sludge was then mixed with water and methyl cellulose and injected into the extruder and cut to a specific size. They were dried at 110 °C for 24 h followed by calcining at 300–600 °C for 4 h to achieve the pellet type sorbents. These sorbents were then employed in a dynamic adsorption test to evaluate the performance for TMA adsorption from gas streams. Results suggest that the sorbent calcined at 500 °C had the TMA removal performance of 8.374 mg/g, which was likely due to the highest percentage of micropore volume and the smallest average pore diameter as well as the acid sites of the sorbent.

Recently, Shen et al. [26] investigated alum sludge mixed with Kaolin clay for ceramsite production and phosphorus (P) removal. Powdery alum sludge, Kaolin clay and water were mixed under different ratios to make pellets, which were sintered from 600 to 1000 °C for 10–60 min. Batch adsorption test indicated that the best P adsorption of 10.2 mg P/g pellet was obtained from the sorbent that contained 40% Kaolin clay while heating at 650 °C for 60 min. Further, Wu et al. [27] reported granular alum sludge adsorbent for P removal. Powdery alum sludge was mixed with organic/inorganic binder and pore-forming agents for pelleting, the resultant pellets were then dried and sintered at 500 °C for 2 h. Results indicated that P adsorption capacity by granular sorbent was 0.9 mg/g when treating the actual tail wastewater.

In addition, Kang et al. [28] examined alum sludge pellet sorbent for arsenic (As) removal. Dewatered alum sludge and molasses were mixed under three different ratios of 1, 3 and 5 wt% and the paste was dried in a dark condition for 5 days. It is worth noting that the moisture of the alum sludge was directly used to prepare the paste without adding water. The paste was dried to 70 wt% moisture and pelletized (0.5–1.5 cm). Thereafter, the pellets were dried at 105 °C for 24 h. The thermal treatment was under three different reaction media of air, N₂ and CO₂ for 3 h to enhance the strength of pellet and to make a porous structure. Batch adsorption results suggested that the pellets thermally treated under CO₂ present the best adsorption performance of As.

2.2. Gel Entrapment of WTRs

Due to its cost effectiveness, gel entrapment using calcium-alginate beads is widely used in immobilization of various powdered materials to remove target pollutants from an aqueous solution [19]. Jung et al. [29] firstly reported a gel entrapment of WTRs for the production of fluoride adsorptive media. Thermal pretreatment (calcinated at 450 °C for 4 h) of alum sludge was added to 2% (*w/v*) sodium alginate solution, and the mixture was stirred for 10 h. Thereafter, it was dropped into 2% (*w/v*) calcium chloride to form particulate under gentle stirring. The resultant pellets were washed and oven-dried at 45 °C for 24 h. Batch and fixed-bed column adsorption trials indicated that the alum sludge sorbent had high removal performance of fluoride (39.59 mg/g) from actual industrial wastewater. Later, Poormand et al. [30] also reported a same gel entrapment method for the production of granular WTRs. However, this study aimed to remove methylene blue from aqueous solutions. Results suggested that the maximum methylene blue sorption capacity of granular WTRs was 909.1 mg/g. Furthermore, Li et al. [18] examined a similar strategy by adding the mixture to 2% (*w/v*) FeCl₃ solution (previous study was calcium chloride). The resultant media was applied for P adsorption with the maximum capacity of 19.70 mg/g. A similar investigation was carried out by Shen et al. [31]. The same gel entrapment method was employed, but the resultant wet pellets were directly used for P adsorption (without drying). Results suggested that the maximum P adsorption capacity of the wet alum sludge bead was 19.42 mg P/g.

Kang et al. [32] also investigated the gel entrapment of alum sludge for As removal. Raw and pretreated alum sludges (calcined at 300 °C for 24 h) were added into 2% sodium alginate, 2% sodium alginate and 1.5% polyvinyl alcohol (PVA), respectively. In total, four kinds of mixtures were dropped into 0.1 M CaCl₂·2H₂O solution and hardened for 48 h. The resultant pellets were dried at 25 °C for 4 h and the raw alum sludge-based sorbents were calcined at 300 °C for 3 h. Results indicated that the calcination of alginate beads could enhance the surface area greatly and also overcome the slow adsorption kinetics of a bead type adsorbent.

Table 1. Various studies regarding WTRs granulation and their applications.

Ref.	Materials	Technique	Sorbent Characteristics				Target Pollutant	Adsorption Capacity
			S _p (BET) (m ² /g)	Total Pore Volume (cm ³ /g)	Average Pore Size (nm)	Compressive Strength (N/mm ²)		
[22,23]	Alum sludge (45%), wastewater treatment sludge (55%), water glass (sodium silicate, 20% of total sludge weight)	Pelletized to 5–8 mm and sintering from 200 to 1000 °C for 35 min	93.7	/	/	15.6	COD & TN	82.2% of COD, 43.9–51.0% of TN
[25]	Pretreated alum sludge (400 g), water (250 g), methyl cellulose (20 g)	Extrusion (diameter 4.5 mm, length 8 mm) and calcined from 300 to 600 °C for 4 h	82–175	0.17–0.51	2.4–3.2	3.6–13.5	Trimethylamine (TMA)	8.374 mg/g (calcined at 500 °C)
[29]	Thermal treated alum sludge (2% <i>w/v</i>), sodium alginate solution (2% <i>w/v</i>), calcium chloride (2% <i>w/v</i>)	Gel entrapment: pretreated alum sludge mixed with alginate solution by dropping into calcium chloride to form particulate and dried at 45 °C for 24 h	98.251	0.14	8.3	/	Fluoride (F)	39.59 mg/g
[18]	Thermal treated alum sludge (10 g), Sodium alginate solution (2% <i>w/v</i>), FeCl ₃ ·6H ₂ O (2% <i>w/v</i>)	Gel entrapment: pretreated alum sludge mixed with alginate solution by dropping into FeCl ₃ solution to form particulate and naturally air-dried	43.8	0.049	2.6	/	Phosphorus (P)	19.7 mg/g
[26]	Alum sludge (60%), Kaolin-clay (40%), water (0.5 mL/g)	Extrusion (5–8 mm) and calcined from 600 to 1000 °C for 10–60 min	/	/	/	/	Phosphorus (P)	10.2 mg/g
[31]	Alum sludge (1–2% <i>w/v</i>), sodium alginate solution (1% <i>w/v</i>), calcium chloride (0.5 mol/L)	Gel entrapment: alum sludge mixed with alginate solution by dropping into calcium chloride to form particulate (3–5 mm)	/	/	/	/	Phosphorus (P)	19.42 mg/g
[21]	Alum sludge (75%), Clay (25%), water	Pelletize balls (6–8 mm) was preheated at 400 °C for 30 min and sintered at 1050 °C for 10 min	4.85	/	/	/	Nutrients in wastewater (NiW)	98.6% of TP, 91.0% of TN, 85.8% of COD
[33]	Waterworks sludge, aluminum slag, gypsum, silica and maifan of 4:4:10:1:1	NaOH solution (1 mol/L) was added into the mixture to obtain spherical granularity and followed by hardening, drying, and natural curing	/	/	/	2 (Mohs hardness)	Phosphorus (P)	2 mg/g

Table 1. Cont.

Ref.	Materials	Technique	Sorbent Characteristics				Target Pollutant	Adsorption Capacity
			S _p (BET) (m ² /g)	Total Pore Volume (cm ³ /g)	Average Pore Size (nm)	Compressive Strength (N/mm ²)		
[28]	Alum sludge (1, 3, 5 wt%), molasses	Mixing alum sludge and molasses and pelletized. Pellets was dried at 105 °C for 24 h (0.5–1.5 cm). Others were thermal treated at 300–400 °C for 3 h under air, N ₂ and CO ₂ (0.3–1.0 cm)	38.9–159.6	/	/	/	Arsenic (As)	28.9 mg/g
[32]	Pretreated/raw alum sludge (10%), Sodium alginate (2%), polyvinyl alcohol (PVA 1.5%), CaCl ₂ ·2H ₂ O solution (0.1 M).	Gel entrapment: pretreated alum sludge mixed with alginate solution (and PVA) by dropping into calcium chloride to form particulate (0.8–1 mm) and dried at 25 °C for 24 h (calcined at air-based for 3 h)	0.3–36.84	/	/	/	Arsenic (As)	26.39 mg/g
[20]	Waterworks sludge, fly ash, river sediment	Sintering ceramicsite (not specify)	8.15	1.88	8.53	/	Nutrients in wastewater (NiW)	70% of COD, 60% of NH ₃ -N, 79% of TP,
[27]	Alum sludge, Na ₂ SiO ₃ , AlCl ₃ , PVA, carboxymethyl cellulose (CMC), NaHCO ₃ , starch.	Alum sludge mixed with organic binder or inorganic binder and pore-forming agents for pelleting, drying and sintering at 500 °C for 2 h	23.12	0.076	13.21	/	Phosphorus (P)	0.9 mg/g
[16]	Alum sludge, PVA	Freeze-thaw process: 10 g alum sludge mixed with PVA solution frozen at −20 °C for 12 h and thawed at room temperature for 4 h, repeated for three cycles. (L × W × H = 5 × 5 × 3 mm)	44.72	0.052	<10	/	Phosphate (P)	23.34 mg/g

2.3. Newly Emerged WTRs Granulation Technique

2.3.1. Natural Curing

In a recent study carried out by Gao et al. [33], a sustainable non-combustion granulation technique for the production of WTRs-based CWs substrate was investigated. The study aimed to overcome the energy consuming problem of the sintering process. Waterworks sludge and aluminum slag were subjected to thermal pretreatment at 105 °C for 2 h. Thereafter, waterworks sludge, aluminum slag, gypsum, silica and maifan were evenly mixed with the ratio of 4:4:10:1:1. NaOH solution (1 mol/L) was continuously added, and the mixture was uniformly stirred to obtain a spherical granularity. The resultant pellets were naturally dried for 2 h and then oven dried at 105 °C for 2 h. Static P adsorption trials suggested that 95% P was removed from the simulated phosphorus-containing wastewater.

2.3.2. Freeze–Thaw Process

In another recent study reported by Li et al. [16], alum sludge was granulated by a freeze–thaw method and the products were applied for P removal. Powdery alum sludge was added into PVA solution and mixed thoroughly. The mixtures were frozen at −20 °C for 12 h and thawed at room temperature for 4 h; this freeze–thaw process was repeated for three cycles. Finally, the resulting samples were washed and air-dried naturally. Results showed that granulation reduced the leaching and bioaccessibility of most metals within the raw alum sludge. Batch adsorption trials indicated that the P adsorption capacity of the granules was 23.34 mg/g.

3. Discussion

3.1. Classification of WTRs Granulation

Figure 2 illustrated the classification of WTRs granulation. From the outermost to the inner annulus, they were classified by pelleting technique, target pollutant, granulation method and reported years. It can be seen that, among the 14 investigations in the literature, 8 studies employed sintering technology, 4 studies employed gel entrapment method, and 2 studies employed novel methods i.e., freeze–thaw process, and natural curing.

Figure 2. Classification of various WTRs granulation studies in literature.

The sintering method was the first and the most popular technology, which has been widely employed at the early stage of WTRs granulation. However, the inherent drawbacks of sintering, e.g., high energy and time consuming, potential environmental pollution risks, hinder its further development [34]. Moreover, sintering could lead to a substantial decrease in the P adsorption capacity due to Al and Fe crystallization [35]. However, Kang et al. [28] state that sintering increased the number of adsorption sites of WTRs through the removal of organic matters and generation of pores on the WTRs surface and also formed a rough surface. Moreover, the oxidation or combustion process under air medium showed a relatively higher adsorption capacity, but the alum particles were released from the pellet.

Later, WTRs gel entrapment was reported to partially replace the sintering ceramsite, but the complex operation process, e.g., thermal pretreatment of alum sludge, gentle stirring to form the pellet, hinders the wide application of the WTRs gel entrapment technique [18]. Thereafter, a natural curing method was examined, which could remedy the high energy consuming of sintering and complex operation of gel entrapment [33]. This method, which utilizes NaOH solution as a binder to mix several materials (e.g., alum slag, gypsum) and the resultant WTRs products, have been used as substrate in CWs. The heavy metal lability and bio-accessibility still need further investigation. Moreover, the recently reported freeze–thaw process seems to still need significant energy as well as chemical binder, e.g., PVA to form the pellet. In particular, the freeze–thaw process needs to repeat three times. Energy and time consumption (almost same as sintering method) are still the big concerns.

Regarding the resultant granular/pellet WTRs applications, P removal was the most commonly reported reuse route. In the literature, there were six studies (among 14 investigations) that reported the granular WTRs for P removal. It is likely due to the fact that WTRs contain a large amount of Al (over 30 wt%), and Al has very strong affinity with P [36,37]. Moreover, there were four studies that examine the removal of nutrients in wastewater, e.g., COD, TN, TP. As the granular WTRs were employed as a media/substrate in CW to overcome the clogging problem when using the raw WTRs, the wastewater was purified mainly through the biological reaction between biofilm, which was developed on the WTRs pellet, and the nutrients in wastewater. Additionally, there were two investigations concerned about As removal, and one study utilized F as target pollutant. It can be concluded from the limited granular WTRs applications, that the adsorption capacity of various pollutants declined after granulation, compared to the raw WTRs. The reason is likely that the granulation process decreased the active sites on WTRs while sintering could also lead to Al and Fe crystallization [34]. In fact, raw WTRs has been proven to remove several heavy metals and semimetals, including Cd, Cr, Co, Cu, Pb, Hg, Ni, Zn, Mo, V, Ga, As, Se, and B [6]. However, from the limited WTRs granulation studies, granular WTRs could only sorb a few pollutants, such as P, As and F. It suggested that various pollutants (e.g., heavy metals and semimetals) should be included in future studies to expand the granular WTRs application. Nevertheless, it is worth noting that only one study reported pellet-type WTRs for gas phase pollutant (TMA) removal [25]. In a recent study, raw alum sludge powder has been successfully reused as an efficient sorbent for H₂S removal from waste gas [11]. Therefore, it is highly recommended to investigate the granular WTRs for various gas phase pollutants, even wastewater treatment plant odor removal. In particular, either reuse of raw WTRs or granular WTRs for waste gas purification is a promising WTRs application route, but few references can be found in the literature, which also needs more ensuing studies to support this application.

In general, granulation process can be divided into two types: wet granulation that utilizes a liquid in the process and dry granulation that requires no liquid [19]. However, it is interesting to note that only one study (among 14 investigations) investigated the dry granulation of the WTRs [28], in which the study utilized the inherent moisture of raw WTRs without adding extra water. In fact, the moisture of raw WTRs cakes was around 80% and further drying would be time and energy intensive [33]. On the contrary, in WTRs wet granulation, raw WTRs cakes were firstly dried in an oven (usually 105 °C for 24 h) and ground into powder, but the resultant dewatered WTRs powders were evenly mixed with binders and water again to form pellets. Therefore, dry granulation method

seems a much wiser choice, which needs more future studies to enhance the feasibility on a larger scale. This approach could directly utilize the inherent moisture of raw WTRs, without the complex drying and pelleting processes of wet granulation.

3.2. Materials in WTRs Granulation

Figure 3 presents 22 kinds of materials which were related to WTRs granulation processes. Their usage frequency was represented by the size of the circle. Among those materials, water was the most widely employed material in the granulation process, since majority of the WTRs studies were based on wet granulation methods. Nevertheless, future investigations of the WTRs pelleting processes could utilize the inherent moisture of raw WTRs. Furthermore, the major components of WTRs are similar to those of clay, but several studies still employed clay in the production of WTRs ceramsite [21,26]. It is suggested that WTRs could replace clay in the sintering ceramsite. On the other hand, future studies still need to explore other materials for replacing clay in ceramsite production to achieve the sustainable development of natural resources as well as the protection of the earth surface environment.

Figure 3. Various materials have been used for WTRs granulation.

Granulation and pelleting always require binders to aggregate particles. Various binders including organic and inorganic binders were also summarized in Figure 3. In literature, the frequently used materials were sodium alginate, PVA, water glass, AlCl_3 , CMC, NaOH, methyl cellulose, molasses. Wu et al. [27] suggested that AlCl_3 was the optimum binder compared to other binders such as Na_2SiO_3 , PVA, CMC. Starch was the best pore-forming agent compared to NaHCO_3 , while the optimum dosage was 4%. It can be concluded from the various studies that the amounts of binders in the pelleting and granulation process could influence the strength and adsorption capacity of adsorbent. The amounts of moisture in the pellets could change the pore structure during the thermal treatment [16,18]. Moreover, various studies also have proven that heavy metals are properly stabilized in WTRs ceramsite and cannot be easily released into the environment again to cause secondary pollution, which is in line with the sustainable development and can be safely reused [22,38].

3.3. Granular WTRs Characteristics

The characteristics, e.g., compositional and structural variations of granular WTRs obtained in the literature, were attributed to many factors, such as sintering temperature, sintering time, kinds of binders and ratios of materials. Figure 4 shows the range of specific surface area and pellet size of granular WTRs in the literature. In general, the calcination process could create a rough surface and increase the surface area and result in enhanced adsorption kinetics [27,28].

Figure 4. The range of Sp (BET) and pellet size of granulated WTRs.

Xu et al. [22] suggested that the optimal contents of SiO_2 and Al_2O_3 in WTRs ranged from 14% to 26% and 22.5% to 45%, respectively, to produce the sintering WTRs ceramsite. The major acidic oxides (Al_2O_3) in WTRs could strongly affect the bloating behavior and crystal formation of the WTRs ceramsite during the sintering process. Meanwhile, Chen et al. [21], Zou et al. [23], and Gao et al. [33] suggested that the well-developed porous structures of WTRs ceramsite have many unevenly-distributed pores ($0.5 \mu\text{m} < \text{pore size} < 10.0 \mu\text{m}$). These pores are theoretically suitable for the attached growth of microorganisms and rougher surfaces with a lot of agglomerated crystals propitious to develop microbial communities and to enhance the biofilm layers. These will benefit the pollutants removal efficiencies. It indicated that the granulate/pellet WTRs are more suitable to be the CWs substrates compared to the raw WTRs cake. Li et al. [18] pointed out that gel entrapment of powdered WTRs had a slight influence on WTRs functional groups and also did not alter the crystalline phase of WTRs. However, gel entrapment granulation could lower the surface area and total pore volume of raw WTRs. Most metals in granular WTRs appear to become more stable with a lower leachability.

It should be noted that only three studies (among 14 investigations) reported the compressive strength data of the WTRs pellet adsorbents. Although many studies have proven that the compressive strength of WTRs pellet was increased after thermal treatment, it is still one of the major concerns for the pellet adsorbents when they were applied in filter media for wastewater treatment. Therefore, it is better to involve compressive strength analysis of granular WTRs in future studies.

4. Conclusions and Prospects

Various WTRs granulation technical and technological innovations can be found in the last twenty years. Granulation and pelleting of WTRs have been applied to increase the size of the adsorbent, in which the specific shape leads to convenient transportation, storage, and utilization. Granular WTRs also exhibited good mechanical stability and reusability which is, no doubt, to broaden the applications of WTRs. Moreover, heavy metals (in spite of the small amount in WTRs) are properly stabilized in granular WTRs and cannot be easily released into the environment again to cause secondary pollution. Thus, it can be concluded that WTRs granulation improved and eased the existing WTRs reuse route and also contributed to WTRs value-added products applications.

Although there were 14 investigations up to now, indicating that studies on this topic are still in their initial developing stage, WTRs granulation techniques and technologies have improved over

the years, but still need further intensive worldwide investigations. Efficient and cost-effective WTRs granulation methods have always been the keen interest of the real engineering applications, which catapults the research and development of new and improved technologies by the interdisciplinary scientists of environmental and chemical engineering globally. To summarize, the future prospects of WTRs granulation are as follows:

1. Alternative options need to be explored to make the granulation technique in a more environmentally-sound manner;
2. Smaller-scale demonstrations need to be carried out to investigate the granular WTRs suitability for larger-scale application;
3. Various pollutants e.g., heavy metals, semimetals and particularly gas phase pollutants should be included in future research to expand the scope of granular WTRs application;
4. WTRs dry granulation is a promising technique which needs further intensive examination to prove its feasibility on a larger scale;
5. It seems necessary to explore other materials for replacing clay in WTRs ceramsite production to achieve the sustainable development of natural resources;
6. It is better to involve compressive strength analysis of granular WTRs in future studies;
7. Overall, this emerging technology for production and utilization of the granular WTRs will experience a large growth in the future, although there are currently limited data available.

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References

1. Zhao, Y.Q.; Liu, R.B.; Awe, O.W.; Yang, Y.; Shen, C. Acceptability of land application of alum-based water treatment residuals—An explicit and comprehensive review. *Chem. Eng. J.* **2018**, *353*, 717–726. [\[CrossRef\]](#)
2. Xu, D.; Lee, L.Y.; Lim, F.Y.; Lyu, Z.; Zhu, H.; Ong, S.L.; Hu, J. Water treatment residual: A critical review of its applications on pollutant removal from stormwater runoff and future perspectives. *J. Environ. Manag.* **2020**, *259*, 109649. [\[CrossRef\]](#) [\[PubMed\]](#)
3. Turner, T.; Wheeler, R.; Stone, A.; Oliver, I. Potential alternative reuse pathways for water treatment residuals: Remaining barriers and questions—A review. *Water Air Soil Pollut.* **2019**, *230*. [\[CrossRef\]](#)
4. Ren, B.M.; Zhao, Y.Q.; Lyczko, N.; Nzihou, A. Current status and outlook of odor removal technologies in wastewater treatment plant. *Waste Biomass Valorization* **2019**, *10*, 1443–1458. [\[CrossRef\]](#)
5. Gomes, S.D.; Zhou, J.L.; Li, W.G.; Long, G.C. Progress in manufacture and properties of construction materials incorporating water treatment sludge: A review. *Resour. Conserv. Recycl.* **2019**, *145*, 148–159. [\[CrossRef\]](#)
6. Shen, C.; Zhao, Y.; Li, W.; Yang, Y.; Liu, R.; Morgen, D. Global profile of heavy metals and semimetals adsorption using drinking water treatment residual. *Chem. Eng. J.* **2019**, *372*, 1019–1027. [\[CrossRef\]](#)
7. Muisa, N.; Nhapi, I.; Ruziwa, W.; Manyuchi, M.M. Utilization of alum sludge as adsorbent for phosphorus removal in municipal wastewater: A review. *J. Water Process Eng.* **2020**, *35*, 101187. [\[CrossRef\]](#)
8. Kumar, R.; Kang, C.U.; Mohan, D.; Khan, M.A.; Lee, J.H.; Lee, S.S.; Jeon, B.H. Waste sludge derived adsorbents for arsenate removal from water. *Chemosphere* **2020**, *239*, 124832. [\[CrossRef\]](#)
9. Shakya, A.K.; Bhande, R.; Ghosh, P.K. A practical approach on reuse of drinking water treatment plant residuals for fluoride removal. *Environ. Technol.* **2019**, 1–13. [\[CrossRef\]](#)
10. Ackah, L.; Guru, R.; Peiravi, M.; Mohanty, M.; Ma, X.; Kumar, S.; Liu, J. Characterization of southern Illinois water treatment residues for sustainable applications. *Sustainability* **2018**, *10*, 1374. [\[CrossRef\]](#)
11. Ren, B.; Lyczko, N.; Zhao, Y.; Nzihou, A. Alum sludge as an efficient sorbent for hydrogen sulfide removal: Experimental, mechanisms and modeling studies. *Chemosphere* **2020**, *248*, 126010. [\[CrossRef\]](#) [\[PubMed\]](#)

12. Ren, B.; Lyczko, N.; Zhao, Y.; Nzihou, A. Integrating alum sludge with waste-activated sludge in co-conditioning and dewatering: A case study of a city in south France. *Environ. Sci. Pollut. Res.* **2020**. [[CrossRef](#)] [[PubMed](#)]
13. Fang, X.L.; Wang, L.; Poon, C.S.; Baek, K.; Tsang, D.C.W.; Kwok, S.K. Transforming waterworks sludge into controlled low-strength material: Bench-scale optimization and field test validation. *J. Environ. Manag.* **2019**, *232*, 254–263. [[CrossRef](#)] [[PubMed](#)]
14. Choi, D.; Oh, J.I.; Lee, J.; Park, Y.K.; Lam, S.S.; Kwon, E.E. Valorization of alum sludge via a pyrolysis platform using CO₂ as reactive gas medium. *Environ. Int.* **2019**, *132*, 105037. [[CrossRef](#)] [[PubMed](#)]
15. Hua, T.; Haynes, R.J.; Zhou, Y.F. Competitive adsorption and desorption of arsenate, vanadate, and molybdate onto the low-cost adsorbent materials alum water treatment sludge and bauxite. *Environ. Sci. Pollut. Res. Int.* **2018**, *25*, 34053–34062. [[CrossRef](#)] [[PubMed](#)]
16. Li, X.; Yu, D.; Su, L.; Pei, Y. Facile method to granulate drinking water treatment residues as a potential media for phosphate removal. *Colloids Surf. A Physicochem. Eng. Asp.* **2020**, 586. [[CrossRef](#)]
17. Hu, Y.; Zhao, Y.; Zhao, X.; Kumar, J.L.G. High rate nitrogen removal in an alum sludge-based intermittent aeration constructed wetland. *Environ. Sci. Technol.* **2012**, *46*, 4583–4590. [[CrossRef](#)]
18. Li, X.Q.; Cui, J.; Pei, Y.S. Granulation of drinking water treatment residuals as applicable media for phosphorus removal. *J. Environ. Manag.* **2018**, *213*, 36–46. [[CrossRef](#)]
19. Shanmugam, S. Granulation techniques and technologies: Recent progresses. *Bioimpacts* **2015**, *5*, 55–63. [[CrossRef](#)]
20. Wang, Y.; Yang, J.; Xu, H.; Liu, C.; Shen, Z.; Hu, K. Preparation of Ceramsite based on waterworks sludge and its application as matrix in constructed wetlands. *Int. J. Environ. Res. Public Health* **2019**, *16*, 2637. [[CrossRef](#)]
21. Chen, S.; Chen, Y.; Pei, H.; Hou, Q. Biofilm development dynamics and pollutant removal performance of ceramsite made from drinking-water treatment sludge. *Water Environ. Res.* **2019**, *91*, 616–627. [[CrossRef](#)] [[PubMed](#)]
22. Xu, G.; Zou, J.; Li, G. Ceramsite made with water and wastewater sludge and its characteristics affected by SiO₂ and Al₂O₃. *Environ. Sci. Technol.* **2008**, *42*, 7417–7423. [[CrossRef](#)] [[PubMed](#)]
23. Zou, J.L.; Xu, G.R.; Pan, K.; Zhou, W.; Dai, Y.; Wang, X.; Zhang, D.; Hu, Y.C.; Ma, M. Nitrogen removal and biofilm structure affected by COD/NH₄⁺-N in a biofilter with porous sludge-ceramsite. *Sep. Purif. Technol.* **2012**, *94*, 9–15. [[CrossRef](#)]
24. Wang, X.; Tian, Y.; Liu, H.; Zhao, X.; Peng, S. Optimizing the performance of organics and nutrient removal in constructed wetland–microbial fuel cell systems. *Sci. Total Environ.* **2019**, *653*, 860–871. [[CrossRef](#)] [[PubMed](#)]
25. Bae, J.; Park, N.; Kim, G.; Lee, C.H.; Park, Y.K.; Jeon, J.K. Characteristics of pellet-type adsorbents prepared from water treatment sludge and their effect on trimethylamine removal. *Korean J. Chem. Eng.* **2014**, *31*, 624–629. [[CrossRef](#)]
26. Shen, C.; Zhao, Y.; Liu, R. Development of pellet-type adsorbent based on water treatment residual. *Desalin. Water Treat.* **2018**, *112*, 3–11. [[CrossRef](#)]
27. Wu, H.F.; Wang, J.P.; Duan, E.G.; Feng, Y.F.; Wan, Z.Y.; Wu, Y.X.; Lu, Y.Q. Study on the preparation of granular alum sludge adsorbent for phosphorus removal. *Water Sci. Technol.* **2019**, *79*, 2378–2386. [[CrossRef](#)]
28. Kang, S.; Choi, J.H.; Park, J.G.; Baek, K. Pellet adsorbent derived from molasses and dewatered alum sludge for arsenic removal. *J. CO₂ Util.* **2019**, *33*, 31–36. [[CrossRef](#)]
29. Jung, K.W.; Hwang, M.J.; Jeong, T.U.; Chau, D.M.; Kim, K.; Ahn, K.H. Entrapment of powdered drinking water treatment residues in calcium-alginate beads for fluoride removal from actual industrial wastewater. *J. Ind. Eng. Chem.* **2016**, *39*, 101–111. [[CrossRef](#)]
30. Poormand, H.; Leili, M.; Khazaei, M. Adsorption of methylene blue from aqueous solutions using water treatment sludge modified with sodium alginate as a low cost adsorbent. *Water Sci. Technol.* **2017**, *75*, 281–295. [[CrossRef](#)]
31. Shen, C.; Zhao, Y.; Liu, R.; Mao, Y.; Morgan, D. Adsorption of phosphorus with calcium alginate beads containing drinking water treatment residual. *Water Sci. Technol.* **2018**, *78*, 1980–1989. [[CrossRef](#)]
32. Kang, S.; Park, S.M.; Park, J.G.; Baek, K. Enhanced adsorption of arsenic using calcined alginate bead containing alum sludge from water treatment facilities. *J. Environ. Manag.* **2019**, *234*, 181–188. [[CrossRef](#)] [[PubMed](#)]

33. Gao, J.; Guo, H.; Zhang, J.; Yang, R.; Gao, J.; Wang, G. Preparation of sustainable non-combustion filler substrate from waterworks sludge/aluminum slag/gypsum/silica/maifan stone for phosphorus immobilization in constructed wetlands. *Water Sci. Technol.* **2019**, *80*, 153–163. [[CrossRef](#)]
34. Zou, J.L.; Xu, G.R.; Li, G.B. Ceramsite obtained from water and wastewater sludge and its characteristics affected by Fe_2O_3 , CaO, and MgO. *J. Hazard. Mater.* **2009**, *165*, 995–1001. [[CrossRef](#)] [[PubMed](#)]
35. Wang, C.; Yuan, N.; Bai, L.; Jiang, H.-L.; Pei, Y.; Yan, Z. Key factors related to drinking water treatment residue selection for adsorptive properties tuning via oxygen-limited heat treatment. *Chem. Eng. J.* **2016**, *306*, 897–907. [[CrossRef](#)]
36. Barakwan, R.; Trihadiningrum, Y.; Bagastyo, A. Characterization of alum sludge from surabaya water treatment plant, Indonesia. *J. Ecol. Eng.* **2019**, *20*, 7–13. [[CrossRef](#)]
37. Ostrom, T.K.; Davis, A.P. Evaluation of an enhanced treatment media and permeable pavement base to remove stormwater nitrogen, phosphorus, and metals under simulated rainfall. *Water Res.* **2019**, *166*, 115071. [[CrossRef](#)]
38. Xu, G.; Zou, J.; Li, G. Stabilization/solidification of heavy metals in sludge ceramsite and leachability affected by oxide substances. *Environ. Sci. Technol.* **2009**, *43*, 5902–5907. [[CrossRef](#)]

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