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Review

Application of Alum Sludge in Wastewater Treatment Processes: "Science" of Reuse and Reclamation Pathways

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Abstract: Alum sludge (AlS) refers to the inevitable by-product generated during the drinking water purification process, where Al-salt is used as a coagulant in the water industry. It has long been treated as "waste", while landfill is its major final disposal destination. In fact, AlS is an underutilized material with huge potential for beneficial reuse as a raw material in various wastewater treatment processes. In the last two decades, intensive studies have been conducted worldwide to explore the "science" and practical application of AlS. This paper focuses on the recent developments in the use of AlS that show its strong potential for reuse in wastewater treatment processes. In particular, the review covers the key "science" of the nature and mechanisms of AlS, revealing why AlS has the potential to be a value-added material. In addition, the future focus of research towards the widespread application of AlS as a raw material/product in commercial markets is suggested, which expands the scope for AlS research and development.

Keywords: adsorption; alum sludge; phosphorus; reuse; waste disposal

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1. Introduction

Environmental issues have received considerable attention in recent years. This is mainly due to a reassessment of the relationship between humans and the environment, which has favored a change in attitudes towards environmental issues and has opened up new opportunities for scientific research. This awareness has led the scientific community to confront the extraordinary development of technological innovation along with the ongoing environmental issues. Purification of raw/source water (derived from the surface water bodies of rivers, lakes, and reservoirs) into drinking water in water treatment plants is a common practice necessary for maintaining human daily activities. It involves the well-known water treatment process consisting of coagulation and flocculation, precipitation, filtration, and disinfection [1,2]. However, it has been noted that the purification processes will inevitably generate residual by-products/waste in the form of water treatment sludge due to the addition of chemical(s) serving as coagulant(s) to accelerate the aggregation of various impurities in raw/source water in the coagulation and flocculation process. Alum and/or ferric salts are commonly used coagulants in practice, while "alum sludge (AlS)" is generated when alum salt is used. Generally, the proportion of AlS is 1–3% of the treated water (in m^3/d) [3]. Due to the increasing demand for clean water with the rapid growth of the world population and urban expansion, the volume of AlS has increased worldwide in recent years. Thus, there is significant concern regarding how to effectively and efficiently manage AlS with the aim of achieving economical savings during its final disposal while maintaining environmental sustainability.

It is now necessary to adopt the "5R" principles (Reduce, Reprocess, Reuse, Recycle, and Recover) of waste management in line with sustainable development [4]. Potential reuse of AlS has been intensively studied in the last two decades, and the majority of studies have explored AlS as a low-cost adsorbent for the remediation of many contaminated water- and soil-borne anions (perchlorate, selenium, and arsenic), including phosphorus (P), fluoride, and heavy metals [3,5–7]. Based on these results, some novel strategies have been developed and implemented, and commercial industrial products made from the AlS have even emerged in recent years on the basis of converting AlS into useful value-added products via granulation [8–10], thus offering more expansive and improved AlS reuse routes. More significantly, the reuse strategies have mainly been developed to target AlS as a useful material in the wastewater treatment process, thus turning AlS as a “waste” into a useful raw material and strengthening the sustainable principle. It should be noted that although AlS is not listed as a harmful “waste” in EU regulations [4,7], its impact on the surrounding environment is also a concern, mainly due to its relatively inert property [11]. Indeed, compared with sewage sludge, AlS is not well studied and its potential levels of reuses are not well understood by the water authorities or even the academic community. Updated research outcomes should be reviewed and delivered via various mediums to attract more attention to bridge the gap between public awareness and the current knowledge. The unique driving force to do so lies in the fact that AlS is a useful material due to its inherent features.

As such, this paper aims to review the AlS studies by reviewing the literature and focusing on the “science” of AlS, then moving on to the potential processes of wastewater treatment that make use of AlS.

2. A Brief Overview of Alum Sludge Study in Bibliometric Analysis

Bibliometric analysis is a useful tool for data analysis. It supplements normal literature reviews to provide an alternative perspective for a literature survey. The most striking feature of bibliometric analysis lies in its knowledge mapping to identify and link key aspects of a certain subject. The performed bibliometric mapping allows for the identification of the most cited items in the literature and the investigation of relationships between the terms obtained [12]. In this paper, a search of the “Web of Science” database using the keywords “waterworks sludge” OR “waterworks residual” OR “alum sludge” OR “water treatment plant sludge” OR “drinking water sludge” was performed, and 516 publications, in scientific journals from 2000 to March of 2021, were obtained.

The bibliometric analysis of the downloaded data was performed on VOSviewer software (https://www.vosviewer.com accessed on 5 March 2021) while version 1.6.15 was used in this study. VOSviewer is a software tool specifically developed for constructing and visualizing bibliometric networks. These networks can be constructed based on key terms and keyword co-occurrence, sources, bibliometric coupling, co-citation, or co-authorship relations. The items are presented as a label and a circle or frame for visualization, while their sizes are dependent on each term’s importance. VOSviewer also offers a text mining functionality that can be used to construct and visualize co-occurrence networks of important terms extracted from a body of scientific literature.

In this study, the key terms analysis processes of Colares et al. [13] were followed with slight adaption. In brief, the bibliometric data were imported into VOSviewer and the terms were extracted from the title and abstract to create a term co-occurrence map based on text data. Based on the software manual, mapping was then carried out after adjusting the parameters in the program. Density visualization is one of the major features of VOSviewer. Overlay visualizations can, for instance, be used to show developments over time.

By using VOSviewer software to analyze the keywords of the papers regarding AlS studies extracted from the literature, the bibliometric mapping of three clusters can be identified. They are AlS sources; waterworks sludge characteristics; and waterworks sludge recycling (Figure 1). In addition, by further analysis of the data, the density visualization of research trends was obtained (Figure 2). In the 2000s, focus was placed on adsorption studies of P and other elements, while in the 2010s, adsorption mechanisms and the development of reuse strategies were the main focus. In the 2020s, energy recovery and carbon footprint reduction for AlS reuse in wastewater treatment processes became more popular in AlS research.

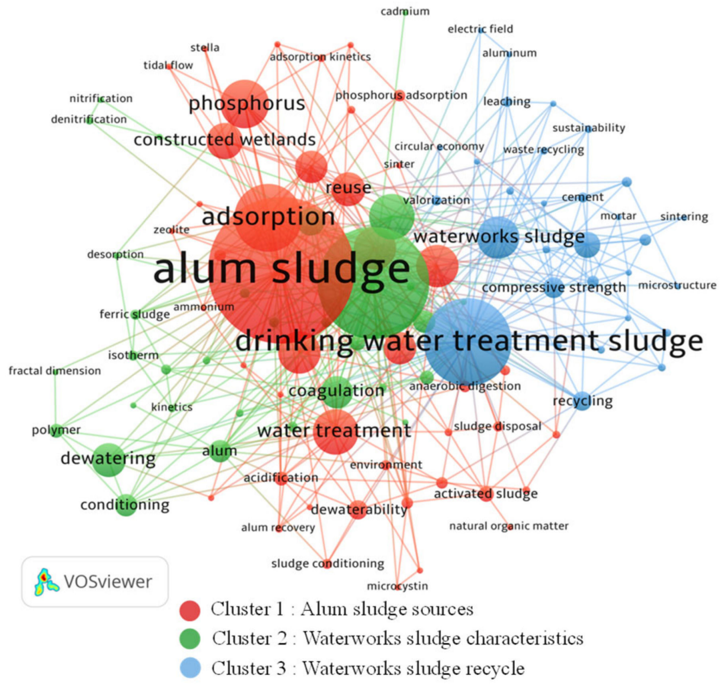

Figure 1. Keyword density visualization of waterworks sludge studies in the last 20 years based on Web of Science search to identify the research clusters.

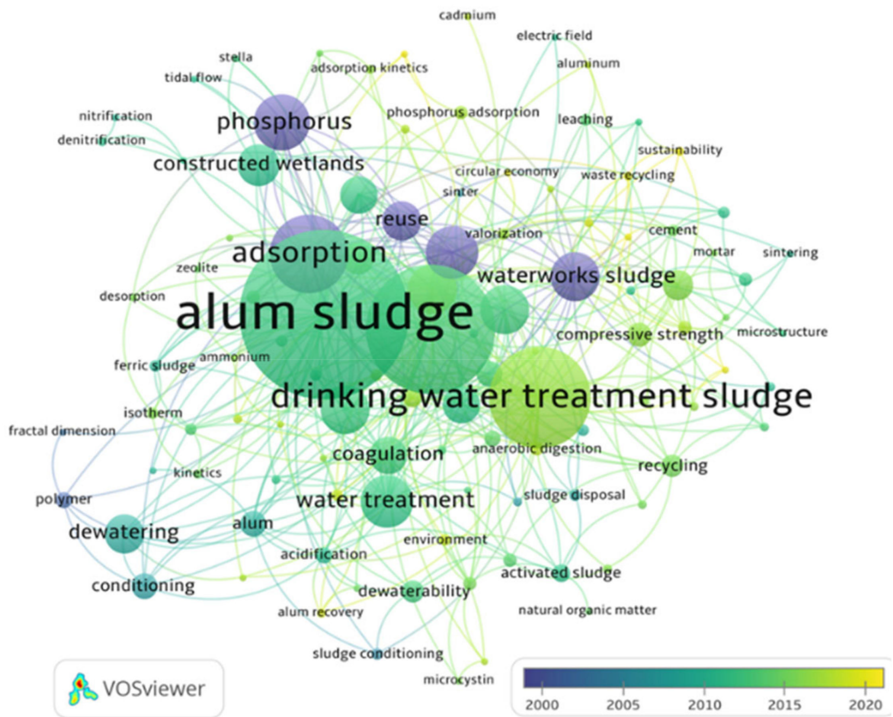

Figure 2. Bibliometric map generated based on density visualization of research trends in the last 20 years.

3. The "Science" Behind Alum Sludge

3.1. Production and Characteristics

The generation of AlS in water treatment plants is from both the sedimentation process (after coagulation and flocculation) and the back washing process during the filtration stage [1,2]. These two streams of sludge are subjected to thickening and conditioning before dewatering to produce the cakes for final disposal [14]. Regarding the amount of AlS, it is difficult to obtain accurate data on its overall generation at the global level; however, China is known to have generated the highest amount at 2.3 million tons per year [7], while, if counted per person, South Korea and Denmark are, respectively, the highest and lowest generators on the global scale [1]. Normally, the AlS is taken to landfill as the primary final disposal point in most countries. The disposal cost in Netherlands stands at a huge sum of US dollar 37–50 million per year while it is US dollar 6.2 million per year in Australia. It is also estimated that the cost of AlS disposal in Ireland will be doubled by the end of the next decade from the present assessment of 15,000–18,000 tons/year of the dried solids, with disposal costs estimated at EUR 2.1 million (US dollar 2.8 million) per year [14–18].

The characteristics of AlS are strongly dependent on the operation of the water treatment plants and the water quality being treated, resulting in differences in the type and concentration of organic matter present in the AlS. However, it is important to note that the AlS is relatively clean, without harmful and toxic elements in most cases, except for the instances where the source water contains specific elements, such as fluoride and arsenic, etc., due to the geological features of the region [5,6]. In fact, AlS is produced with various impurities and contaminants, such as clay minerals, sandy and loamy particles, organic matter, microorganisms, and trace heavy metals, as well as the Al-salt residual, depending on the source water. In general, SiO_2 constitutes the majority of the sludge, followed by Al_2O_3. Other oxides, such as Fe_2O_3, CaO, MgO, Na_2O, K_2O, P_2O_5, and TiO_2, are also found in small percentages in AlS [14]. Table 1 summarizes the physicochemical composition of the AlS from the literature, while Figure 3 jointly presents the X-ray powder diffraction (XRD) and attenuated total reflection–Fourier transform infrared (ATR-FTIR) spectra and scanning electron microscope (SEM) images of the AlS samples [19].

Table 1. Physicochemical composition of AlS [1,14,20–23].

Parameter	Units	Al-Sludge	Parameter	Units	Al-Sludge
pH		6.5 ± 0.3 [a]	Mn	mg/kg	2998 ± 1122
Total solids	mg/L	3800 ± 1385	Zn	mg/kg	98 ± 31
Al	mg/kg	118,700 ± 24,260	Cu	mg/kg	624 ± 581
Fe	mg/kg	37,000 ± 19,740	Ni	mg/kg	28 ± 10
Ca	mg/kg	10,360 ± 4299	Pb	mg/kg	22 ± 12
Mg	mg/kg	2407 ± 572	Cr	mg/kg	20 ± 7
Na	mg/kg	355 ± 142	Cd	mg/kg	0.12 ± 0.02
K	mg/kg	3547 ± 582	Hg	mg/kg	0.46 ± 0.11
S	mg/kg	6763 ± 2955			

[a] Numbers are means ± SD.

3.2. Adsorption of Various Pollutants

A large number of studies have demonstrated AlS' ability and considerable capacity as a low-cost adsorbent for P immobilization [1–3,14,17,21,24]. In addition, other elements of contaminants in wastewater have been tested for adsorption by AlS in recent years. Zhao et al. [5] reported the use of AlS for arsenic immobilization, finding that the maximum adsorption capacities ranged from 0.61 to 0.96 mg-As/g when the pH of the arsenic solution was varied from 9.0 to 4.0. Li et al. [6] investigated modified AlS (pyrolysis and hydrochloric acid treatment) for fluoride immobilization and found that the maximum adsorption capacity could be up to 0.14 mg/g, while the fluoride removal rate could reach 81.2%. In another study, Shakya et al. [16] also used AlS for fluoride removal from an initial quantity of 5.0 mg/L to approximately a 90% reduction within 2 h. More recently, Dias et al. [25]

investigated the removal of two endocrine-disrupting compounds, 17β-estradiol and 17α-ethinylestradiol, by water treatment plant sludge without any modification. The results provide evidence that the sludge allowed the achievement of a considerably higher, up to a complete, removal of these hormones, which emerged as pollutants with a considerable environmental threat. Meanwhile, studies of varied scales have explored the ability and capacity of AlS for the adsorption of a number of heavy metals and semimetals, which include Cd, Cr, Co, Cu, Pb, Hg, Ni, Zn, Mo, V, Ga, As, Se, and B. Shen et al. [7] conducted a comprehensive review on this aspect, with adsorption capacities being reported. These studies have demonstrated the effectiveness of water treatment sludge/AlS as a considerable low-cost adsorbent method for the removal of a wide range of pollutants from wastewater, thus expanding the scope and benefits of the water treatment sludge reuse regime. It should be noted that the AlS is normally subject to air-drying, then ground, and sieved before adsorption tests.

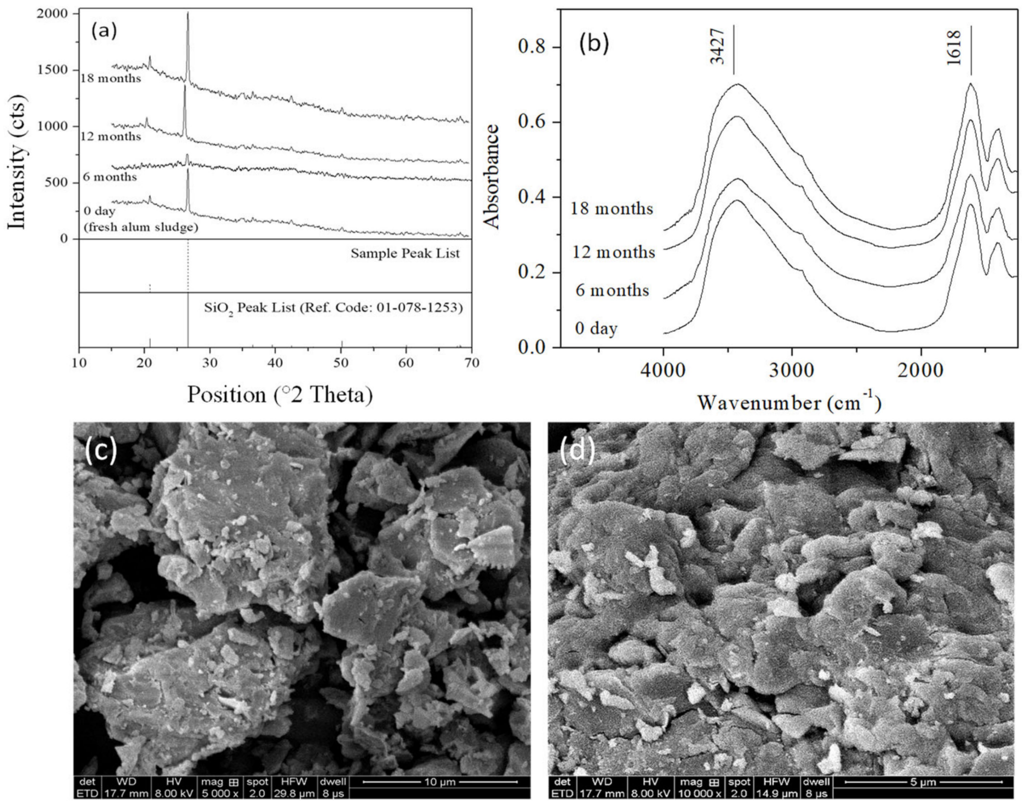

Figure 3. XRD (**a**) and attenuated total reflection–Fourier transform infrared (**b**) spectra of Alum sludge (AlS) samples with ageing times and scanning electron microscope images of AlS with magnitude of 5000 (**c**) and 10,000 (**d**).

3.3. Capacity and Mechanisms of Phosphorus Adsorption

The reuse of dewatered AlS as low-cost adsorbent for P immobilization has been the focus of a large number of investigations in the past [1,3,14,17,21,24–26]. Intensive static and column tests were conducted and adsorption behavior was investigated in great detail across the world [27,28]. The reported maximum P adsorption capacity by AlS is a wide range of 2.02–113.22 mg PO_4^{3-}/g dry sludge [7]. It should be noted that the P adsorption capacity may be linked with the experimental conditions, including pH, sludge particle size, initial P concentration, etc., while caution should be paid when comparing it between different studies [3].

Studies have been conducted to fully characterize AlS through a complete textural characterization and surface chemistry evaluation to identify surface functional groups and also to perform kinetic and equilibrium assays to elucidate the adsorption mechanisms.

It has been well demonstrated that AlS has a strong affinity with P, while ligand exchange is the dominant mechanism based on exploratory evidence of the adsorption mechanism of P [29]. The entire adsorption mechanisms include surface precipitation, ligand exchange, electrostatic attraction, inner-sphere bidentate surface complexation, outer-sphere complexation, and ion exchange [2,17,29], which are illustrated in Figure 4. It should be noted that although a chemical reaction between phosphate and dissolved aluminum has been demonstrated, it is believed that the chemical reaction plays only a marginal role in the phosphate removal process [29].

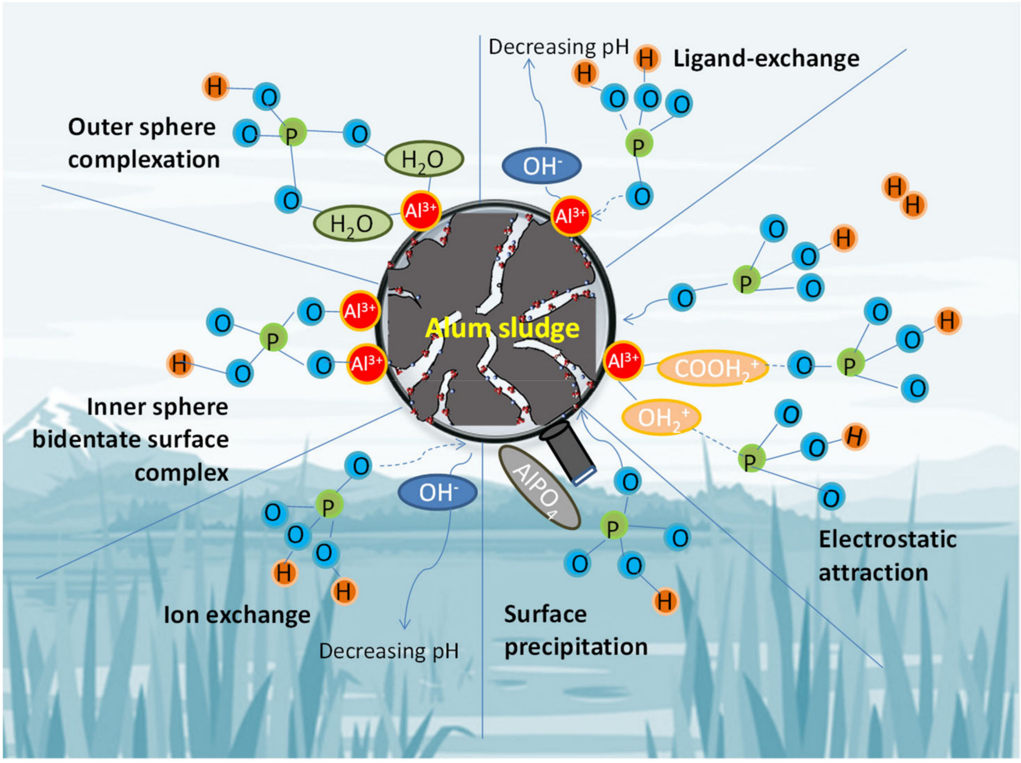

Figure 4. Schematic overview of potential P adsorption mechanisms by AlS [2,17,29].

4. Practical Reuse Tactics in Various Wastewater Treatment Processes

Water contamination is a global challenge impacting both the environment and human health, with significant economic and social costs. The growing scarcity of usable water resources requires effective treatment of wastewater. In this context, the development of cheaper, safer, and more efficient wastewater treatment technologies is urgently needed. In common practice, waste management in terms of landfills, incinerators, treatment, and integrated waste disposal systems is an integral part of our daily lives. The demographic increase, scarce availability of space, and more strict regulations have constrained landfills, thus ruling out landfilling as a conventional final disposal option and necessitating the development of beneficial reuse methods. One promising approach that many studies have reported to be successful has been the reuse of the AlS in water and wastewater management via various treatment processes. The most important driving force is that the AlS is an easily, largely, and locally available by-product and "free of charge", with no harmful elements inside [14]. When AlS is involved in wastewater treatment processes, it represents the concept of using "waste" for wastewater treatment. The sustainable management of the large volume of AlS has motivated water and environmental researchers towards several reuse options after exploring the fundamental "science" behind the AlS. The conceptual action to develop AlS reuse tactics is shown in Figure 5.

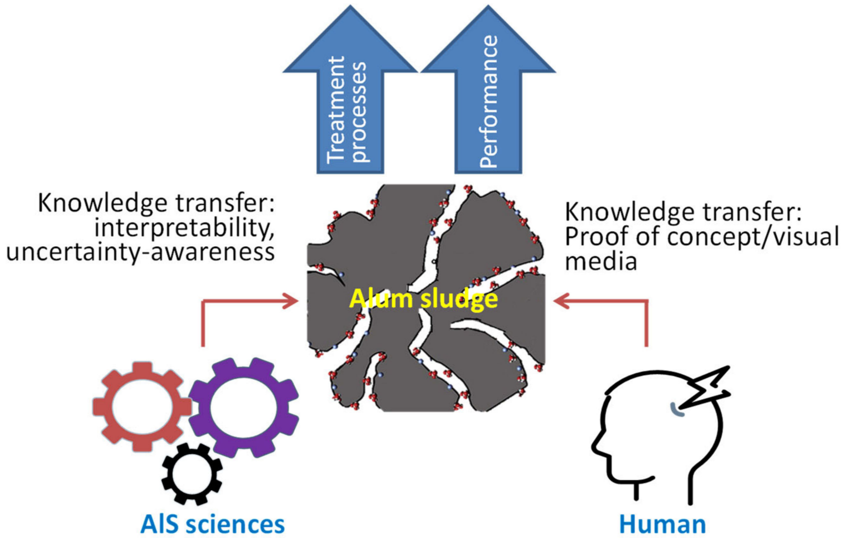

Figure 5. Conceptual patterns of knowledge transfer: from science to engineering of AlS reuse.

4.1. Reuse of AlS in Liquid Form

4.1.1. As Coagulant for Wastewater Treatment

AlS is initially generated in water treatment plants as a liquid stream from the sedimentation tank and filtration tank (via back washing) [30]. For better and more convenient final disposal, AlS is subjected to dewatering to significantly reduce its volume (becoming cake). Thus, reused AlS can either be in liquid form or in dewatered cakes. Studied have demonstrated that AlS in liquid form can be used as a coagulant in wastewater for achieving enhanced primary treatment due to its abundant content of Al^{3+} [14,31]. It has also been used as a special coagulating and flocculating agent for industrial effluent purification [32]. Hu et al. [33] used liquid AlS as a coagulant for pesticide immobilization in wastewater, while Mazari et al. [34] introduced liquid AlS into the pre-treatment process as the primary coagulant for the ultrafiltration (UF) membrane process of municipal wastewater treatment. Shrestha et al. [35] also used waterworks AlS in pilot sewers for the first time to replace chemical coagulants. Recently, Kang [36] investigated the use of liquid AlS in animal farm wastewater treatment as this type of wastewater is a major concern due to the high concentration of chemical oxygen demand (COD) and suspended solids (SS). Treatment of such strong wastewater needs a significant reduction in the pollutants during the primary stages, e.g., coagulation/flocculation and sedimentation, before biological treatment. The removal efficiencies of TSS (total suspended solids), PO_4^{3-}, and TOC (total organic carbon) of 87.76 $\pm$ 2.2%, 96.88 $\pm$ 2.9%, and 62.14 $\pm$ 1.8%, respectively, were obtained; thus, this provides a cost-effective way for high strength wastewater coagulation [36].

4.1.2. As Conditioner for Sewage Sludge Co-Conditioning and Dewatering

Liquid AlS has been employed for sewage sludge co-conditioning and joint dewatering to achieve the dual goals of polymer (conventional conditioner) saving and P control from the rejected water. Yang et al. [37] conducted a study on the co-conditioning and dewatering of an Irish AlS with sewage sludge in Dublin, Ireland, demonstrating that the AlS could improve sewage sludge's dewaterability. The technical foundation was sound, while simultaneous benefits were observed in savings of polymer dosage and control of P in the filtrate from the mechanical dewatering process in the sludge treatment unit in the wastewater treatment plant (WWTP). Taylor and Elliott [38] reported the co-conditioning and dewatering of AlS with sewage sludge, which reduced the amount of polymer dosage so that the total cost of sludge treatment was decreased. More recently, Ren et al. [39] demonstrated the use of a French liquid AlS in co-conditioning and dewatering with sewage sludge from a nearby WWTP. An integrated, cost-effective evaluation of process capabilities was also conducted and the benefit of the joint conditioning and dewatering was obvious, indicating that it is capable of being implemented in practice.

4.2. Reuse of AlS Cakes as Substrate in Constructed Treatment Wetland

Constructed wetland (CW) represents a "green" technology for wastewater treatment and has gained great popularity in the last two decades. Use of dewatered AlS as the main wetland substrate to expand the scope of CW for enhanced wastewater treatment represents an excellent example of the beneficial reuse of AlS [40–45].

Here, it is important to note that CW is a biofilm-based wastewater treatment technology in which wetland substrate plays a vital role towards the success of the treatment system. Substrate as a carrier for biofilm development is the foundation of the CW [44]. Developing new materials as substrates in CW with high adsorption ability and capacity of P and other pollutants is the priority in CW development. AlS has been well studied to be used as the main wetland substrate for P-rich wastewater treatment [40,41,46,47]. A field pilot-scale trial of an AlS-based four-stage CW system was conducted for high-strength farmyard wastewater treatment. Excellent pollutant removal efficiencies have been reported and well accepted by global CW researchers [48].

More significantly, the AlS-based wetland system has been integrated with a microbial fuel cell (MFC) to develop an MFC–CW system to simultaneously achieve the dual goals of wastewater treatment and bioelectricity generation [49–52]. Indeed, the embedding of MFC into AlS-based CW represents a significant development in CW systems in recent years. This allows the CW to be upgraded as a wastewater treatment facility while also being a power producer. Xu et al. [50] reported that the NH4-N removal efficiency could be increased from 44.63 ± 2.07% to 81.10 ± 2.07% in a multiple-cathode MFC–CW. Ren et al. [52] investigated a hybrid two-stage MFC–CFW system for swine wastewater treatment and electricity generation, while Yang et al. [53] recently reported a two-tiered MFC–CW system with pyrrhotite and alum sludge as wetland substrates. Ji et al. [12] recently provided an updated bibliometric analysis of the MFC–CW development.

4.3. Novel Use of AlS for H2S Purification

Dewatered AlS has recently been investigated for hydrogen sulfide (H_2S) adsorption [54]. This is the first time that AlS has been used for gas purification. H_2S is one of several odorous gases arising from industrial effluents such as municipal WWTPs, landfill sites, and petrochemical industries [55]. The average odor threshold of H_2S is reported at 7 to 9 ppb [56]. In a lab-scale fixed-bed column investigation conducted by Ren et al. [54], H_2S adsorption onto AlS was examined and the AlS adsorption capacity was determined to be 374.2 mg of H_2S/g. This demonstrated that AlS could be a cost-effective, largely available, and efficient sorbent for H_2S removal, thus indicating a novel option for H_2S removal using "waste". This novel use of AlS carries good potential for application in WWTPs as the unpleasant odor from wastewater treatment processes has long been a complaint of the public and a major concern of wastewater treatment authorities. It has been found that, compared with other materials, AlS is a promising by-product and a cost-effective option for H_2S control. Undoubtedly, the direct utilization of AlS for H_2S removal has attracted intensive research interest and will be further studied for practical application purposes.

4.4. Granulation

It may be wiser to use AlS as a granular commercial adsorbent for better practical reuse. In recent years, granulation of AlS have been increasingly studied. Granulation is a technique of particle enlargement by agglomeration. It is one of the most significant and commonly used operations in the production of pellet/granular forms from fine or coarse AlS particles, which are converted into large agglomerates [8,57]. These resulting pellets are easy to transport, use, and separate from the adsorption process and are more suitable to be used in wastewater treatment facilities, such as in beds, columns, and filters, due to their increased compressive strength and hydraulic conductivity [58,59]. Therefore, granulation could widen AlS reuse routes and also seems to be a promising strategy to promote widespread engineering application. The current approaches of granulation methodologies are classified into three broad categories: sintering AlS ceramsite [9,60], gel entrapment [61], and newly emerged techniques, e.g., freeze–thaw processes [62] and natural curing [63]. The resultant AlS granulation via encapsulation and sintering can be seen in Figure 6. Shen et al. [64] have produced AlS balls and used them as media in a floating treatment wetland for a comparative study to examine enhanced wastewater treatment behavior. Ren et al. [10] have reviewed the most recent developments in AlS granulation. Undoubtedly, these efforts have successfully demonstrated the potential of AlS as a novel value-added product.

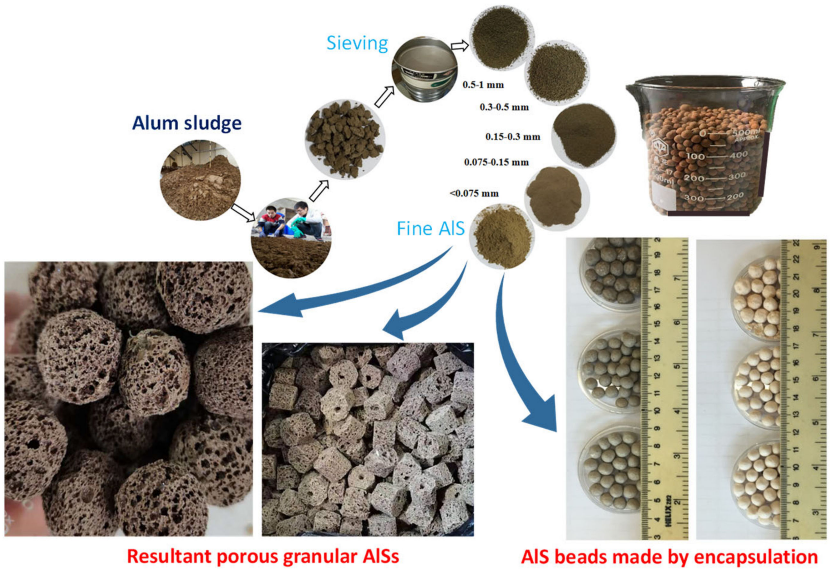

Figure 6. The resultant AlS granulation via encapsulation and sintering.

5. Implications for the Future

The rapid progress of research in AlS sciences has shown its growing potential for implementation in various wastewater treatment processes. The mechanisms behind these studies are the high content of Al ions, large specific surface area, certain pore volumes and porosity of AlS, as well as its wide availability across the world. The oxide or hydroxide in AlS can perform with a strong capacity as a coagulant or adsorbent for a number of pollutants in wastewater [32]. Thus, the development of strategies for its various reuse applications is an urgent priority for the future. Although, more work is currently being done, AlS is still an underutilized material as landfill remains the major final disposal route in the current global situation. Hence, converting raw AlS into useful value-added products via granulation is of great interest worldwide and should be further studied [10]. It is expected that various commercial products based on AlS should be in the market in the near future, thus offering wider and more practical AlS reuse routes and further invigorating water and environmental engineering. It should be pointed out that due to the source water properties and treatment processes in water treatment plants across the world, AlSs have varied characteristics and thus research on the characterization of AlS should be a research priority before any kind of reuse development. In addition, regulations regarding AlS final disposal and reuse should also be updated to consider the recent studies and developments regarding beneficial reuse strategies [11].

To date, except for the reuse routes in wastewater treatment processes, there are other reuse categories, such as reuse of dewatered AlS as building/construction materials or as a partial replacement for clay in clay brick manufacturing as well as in cement production [27,65]. In addition, land-based applications, which comprise the wide range of areas related to agriculture, forestry, and gardening, are also good alternatives for reuse and are worth further investigation and application [11,30].

6. Conclusions

As a long undervalued material, AlS is a water industry by-product without toxic elements and heavy metals. Indeed, it has huge potential for beneficial reuse as a raw material in water and environmental engineering for wastewater treatment due to its large content of Al ions as a coagulant residual. This paper outlines and discusses several novel reuse strategies involved in wastewater treatment processes developed in recent years. These include reuse as a low-cost adsorbent; as the main substrate in constructed treatment wetlands; as a primary coagulant for high-strength wastewater treatment; as a conditioner for co-conditioning/dewatering with sewage sludge; and as a novel material for H_2S/odor gas purification, thus transforming it from "waste" into a value-added product and contributing to sustainable development. The most important feature of AlS is its good adsorption ability of P and other contaminants, while the "science" of its mechanisms has been well investigated, with ligand exchange being the predominant process. From a practical or engineering application point of view, AlS granulation towards commercial products is suggested for future study.

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