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Perspective

Superparamagnetic Iron Oxide Nanoparticles as Additives for Microwave-Based Sludge Prehydrolysis: A Perspective

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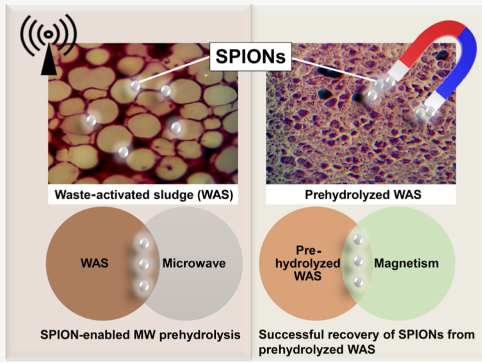
ABSTRACT: Wastewater treatment plants are critical for environmental pollution control. The role that they play in protecting the environment and public health is unquestionable; however, they produce massive quantities of excess sludge as a byproduct. One pragmatic approach to utilizing excess sludge is generating methane via anaerobic digestion. For this, a prehydrolysis step can significantly improve digestion by increasing biogas quality and quantity while decreasing final sludge volumes. One of the many prehydrolysis approaches is to deliver heat into sludge via microwave irradiation. Microwave-absorbing additives can be used to further enhance thermal degradation processes. However, the implications of such an approach include potential release of said additive materials into the environment via digested sludge. In this perspective, we present and discuss the potential of superparamagnetic iron oxide nanoparticles (SPIONs) as recoverable, hyperreactive microwave absorbers for sludge prehydrolysis. Due to their size and characteristics, SPIONs pack spin electrons within a single domain that can respond to the magnetic field without remanence magnetism. SPIONs have properties of both paramagnetic and ferromagnetic materials with little to no magnetic hysteresis, which can enable their rapid recovery from slurries, even in complicated reactor installations. Further, SPIONs are excellent microwave absorbers, which result in high local heat gradients. This perspective introduces the vision that SPION properties can be tuned for desirable dielectric heating and magnetic responses while maintaining material integrity to accomplish repeated use for microwave-enhanced pretreatment.



KEYWORDS: *SPIONs, nanotechnology, anaerobic digestion, microwave pretreatment, renewable energy*

1. OVERVIEW OF SPION-AUGMENTED MICROWAVE-BASED SLUDGE PREHYDROLYSIS

Municipal wastewater treatment plants (WWTPs) generate millions of metric tons of excess biosolids annually in the U.S.[1−3] The transportation and disposal costs of the sludge comprise half of the total wastewater treatment cost, exceeding \$2 billion yr^{-1} with a steady 1% annual increase (mainly due to urbanization and population growth).[4,5] To stabilize excess sludge, anaerobic digestion (AD) is commonly used, which biochemically transforms organic sludge constituents into biogas. In the U.S., over 1200 WWTPs have anaerobic digesters that digest 7.3 million metric tons of excess sludge annually to produce biogas.[3,6] Of note, biogas is a valuable (by)product, and it has comparable calorific significance to natural gas (i.e., biogas: 20−26 kJ L^{-1} vs natural gas: 39 kJ L^{-1}). Furthermore, digested sludge (or digestate) becomes easier to dewater, transport, and dispose. However, even under typical retention times of 20−30 days, decomposition of sludge in AD is incomplete, leaving 35%−45% of organic matter undigested.[7−12] This inefficiency is attributed to the rate-limiting hydrolysis step,[4,13−19] which precedes acidogenesis, acetogenesis, and methanogenesis.[16,20−23]

During hydrolysis, complex insoluble substrates composed of proteins, polysaccharides, and lipids are hydrolyzed into simple soluble components via extracellular enzymes secreted by hydrolytic microorganisms. The key obligate or facultative anaerobes involved in the hydrolytic phase include *Clostridium*, *Cellulomonas*, *Bacteroides*, *Succinivibrio*, *Prevotella*, *Ruminococcus*, *Fibrobacter*, *Firmicutes*, *Erwinia*, *Acetovibrio*, and *Microbispora*.[24,25] Upon the bacterial colonization on the solid surfaces, different enzymes including cellulase, cellobiase, xylanase, amylase, protease, and lipase are released into the matrix producing monomers to be utilized by the hydrolytic bacteria. Lastly, the solid surface is degraded by bacteria.[24,26] The entire process takes place within a few hours for the conversion of carbohydrates to simple sugars and a few days for proteins and lipids to hydrolyze into amino acids and long-chain fatty acids, respectively. On the contrary, the hydrolysis

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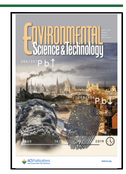

of lignin and lignocellulose, which makes up 25%−35% of sewage sludge occurs slowly and incompletely.[27−29] Sewage sludge is a complex semisolid mixture containing microbial aggregates, filamentous bacterial strains, organic and inorganic particles, extracellular polymeric substances (EPS), and a large quantity of water. EPS, constituting the primary organic component of sludge, exists in three different forms based on their distribution within the sludge matrix: slime EPS is evenly distributed in the liquid phase; loosely bound EPS is a highly porous and dispersible structure; and tightly bound EPS adheres to the surface of bacterial cells. These gel-like, three-dimensional polymers play a crucial role in protecting against cell rupture and lysis, which affect the overall integrity, strength, flocculation, dewaterability, and biodegradability of sludge.[25,30] In addition to EPS, the semirigid structure of the cell walls composed of glycan strands are interconnected by peptide chains resulting in resistance to biodegradation.[31] As a result, sewage sludge with high EPS and cell content has a complex structure, making it more challenging to hydrolyze and digest in the further stages.[25] Therefore, expediting the hydrolysis step by an engineered pretreatment method has been accepted as a practical implementation to improve the efficiency of AD.[32,33]

In recent years, several sludge prehydrolysis methods have been developed and integrated into full-scale WWTPs in the U.S. and around the world, including thermal, ultrasonic, and electrocatalytic approaches.[25,34−37] Some of these full-scale applications are in regions that have a large capacity of anaerobic digestion, but some regions may benefit from enhanced prehydrolysis of anaerobically digested sludge (Figure 1). In principle, sludge prehydrolysis aims at enhancing

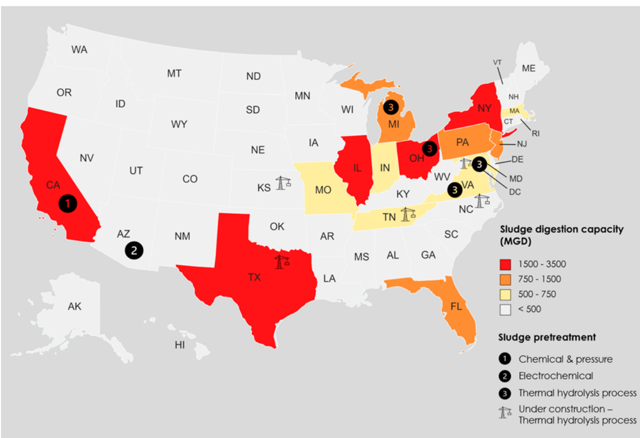

Figure 1. Spatial distribution of sludge digestion capacity of WWTPs in the U.S. Full-scale pretreatment facilities integrated to anaerobic digesters are marked on the map with black circles.[44−48] This map was created with the permission of MapChart.

organic matter (bio)availability by breaking cell walls and disrupting sludge floc assemblies; however, chemical complexity of the sludge matrix and abundance of water limit the selectivity and energy efficiency of pretreatment processes. Therefore, microwave (MW) heating has gained increasingly interest as an alternative thermal pretreatment approach as it provides selective and rapid heating and has been recognized as a versatile and scalable heating alternative for decades.[38,39] Particularly, MWs promote solubilization (∼0.1%−2% soluble chemical oxygen demand, sCOD increase per kJ of MW energy)[38] by (i) breaking down the microfloc assemblies to release extracellular polymeric substances, (ii) disintegrating cell walls to release intracellular organic matter, and (iii) degrading complex molecules into simpler monomers and oligomers. As a consequence, AD of sludge shows increased biogas quality (e.g., 20% improvement in fuel quality),[40] decreased digestate production (e.g., 60%−65% solid reduction),[41] improved dewaterability,[41] improved pathogen removal (e.g., 4.2 log fecal coliforms inactivation),[42] and enhanced kinetics (e.g., 40% increase in digestion rates).[43]

Efficiency of MW prehydrolysis can be improved further if lossy (i.e., large dielectric loss tangent) susceptors such as superparamagnetic iron oxide nanoparticles (SPIONs) can interact with cell walls or floc assemblies during MW irradiation as they effectively convert MWs into heat, creating local hot spots. Consequently, these hot spots can thermally hydrolyze sludge components directly or indirectly via formation of reactive oxygen species (ROS) (Figure 2).[49−51]

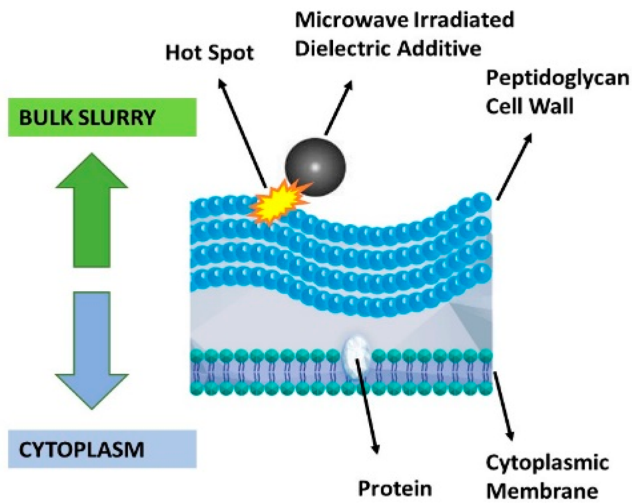

Figure 2. SPION hot spots created by microwave reactivity on cell walls schematic description.

This mechanism involves ferrous ions (Fe^{2+}) at the surface of SPIONs to react with hydrogen peroxide (H_2O_2) and oxygen to produce hydroxyl radicals and ferric ions (Fe^{3+}) via Fenton reaction.[52] SPIONs could also induce friction and physical shear on sludge components through two different mechanisms: (i) vibrating in response to MW radiation and (ii) aggressively moving toward magnetic poles during the magnetic separation stage. However, adding dielectric nanoscale susceptors to waste-activated sludge (WAS) can raise concerns about negatively affecting subsequent AD or having longer-term environmental and public health implications unless recovered from sludge prior to final disposal.

In literature, adding magnetic nanoparticles into anaerobic digesters has shown dosage-dependent stimulation of methane production as they provide essential nutrients, promote direct interspecies electron transfer (DIET), provide active sites for microorganisms, and mitigate the accumulation of inhibitory compounds in digesters.[53−55] Given that AD is a complex multistage process, the way different trophic groups interact with each other significantly impacts the overall effectiveness of the process. An imbalance in hydrogen partial pressure during interspecies electron transfer (IET) between fatty acid oxidizers and hydrogenotrophic methanogens via electron

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carriers (i.e., hydrogen or formate) causes volatile fatty acid (VFA) accumulation and the failure of the AD process. The direct transfer of electrons from exoelectrogenic VFA degraders to electron-capturing methanogens through shared physical and electrical connections eliminates the need to produce redox mediators and thus is more energy-efficient compared to IET.[56,57] DIET is one of the major cell-to-cell electron pathways for syntrophic microorganisms and is mediated by the incorporation of magnetic nanoparticles such as magnetite and hematite.[58] Owing to their conductive nature, magnetite nanoparticles bridge cell connections and foster the DIET mechanism through the formation of cell–magnetite aggregates.[56] Furthermore, given their large specific surface area and surface reactivity, iron-based nanoparticles can also precipitate excess quantities of ammonia, phosphorus, sulfate, and heavy metals. For example, the immobilization of free sulfate by the production of ferrous sulfite and pyrite decreases the population of sulfate-reducing bacteria and hence the hydrogen sulfide content of the produced biogas.[54]

Despite possible advantages, complete recovery of SPIONs is still critical, because the presence of magnetic nanoparticles can harm the organisms by damaging the cell membrane, interrupting electron transport, and releasing toxic components or ROS. ROS formation represents a major toxicity mechanism linked to nanoparticles, wherein elevated levels of ROS can potentially induce oxidative stress, inflammation, and cell death.[59] Furthermore, high concentrations of Fe^{2+} can cause complex formation with free phosphate ions or thiol groups, which hinder the uptake of phosphorus and sulfite by methanogens. However, considering that SPIONs are insoluble at neutral pH, the release of ferric and ferrous ions would be slow.[54] This perspective, instead, introduces two novel considerations regarding the use of nanoparticles for conventional prehydrolysis and anaerobic digestion practices that have not been previously explored. A thorough implementation of this perspective promotes the benefits associated with size-dependent properties of nanoparticles, which are the MW reactivity and magnetizability. Stress conditions induced by MW reactive SPIONs only occur during the prehydrolysis stage, which facilitates the disintegration of WAS cells. These conditions are then diminished by the magnetic separation of SPIONs before solubilized WAS meets the seed microorganisms.

SPIONs are novel nanomaterials with remarkable application potential in a multitude of industries (such as biomedicine).[60−62] Their inherent properties including superparamagnetism, hyperthermia, biocompatibility, and high surface area make them exceptional candidates for sludge pretreatment applications.[62,63] Designed correctly, they have the potential to bind to cells in floc assemblies and be a source of immediate and intense MW heating. In simple terms, MW irradiation creates an oscillating electromagnetic field that causes SPIONs to have both their electrical dipole moments and their magnetic moments rotate, creating internal vibrations that dissipate energy in the form of heat.[64−70] In addition, MW heating with magnetite (Fe_3O_4) SPIONs have been shown to denature proteins and facilitate protein enzymatic degradation[64] and degrade organic water pollutants,[67,68] and thus, degrading and solubilizing complex cell floc assemblies in WAS is plausible. After prehydrolysis, SPIONs can be recovered from slurries magnetically and facilitate their sustainable application in practice, especially some iron oxide forms such as magnetite (Fe_3O_4)[64−70] owing to the superior room-temperature saturation magnetization (∼100 J T^{-1} kg^{-1}) compared to other ferrite materials (e.g., hematite, maghemite: 1−80 J T^{-1} kg^{-1}).[71] This perspective explores the unique potential of SPIONs as applied dielectric susceptors with magnetic recovery potential for enhanced wastewater treatment, i.e., specifically sludge prehydrolysis, with transformative application potential in the wastewater industry.

2. SPION SYNTHESIS, KEY PROPERTIES, AND MAIN BARRIERS IN FRONT OF APPLICATION

SPIONs are ferromagnetic nanomaterials, which are often iron oxide based (e.g., Fe_3O_4, magnetite or γ-Fe_2O_3, maghemite).[72] Superparamagnetism is observed when the size of the ferromagnetic single domain crystal is small enough that, when below the Curie temperature, there is no net material magnetism unless a magnetic field is directly applied, whereby the material then behaves in a paramagnetic fashion and the magnetic moment of the entire crystal aligns.[73,74] In other words, SPIONs have zero magnetization in the absence of an external magnetic field (i.e., not magnetically aggregated with each other) but maintain large magnetic susceptibility when a field is toggled "on", which allows for SPION physical control and thus separation.[73,74] In addition to unique magnetic properties, SPIONs are excellent absorbers of MW radiation through the process of ferromagnetic resonance, which is dissipated as thermal energy to the surrounding matrix with high efficiency.[35] These properties are also strongly dependent on particle size and atomic order (<25 nm), as others have reported.[75] Further, to achieve successful environmental, aqueous-based applications, SPION synthesis should ensure particle stability and dispersity over a range of dynamic heating conditions and specific surface functionality.[76,77]

SPIONs are found in natural and built environments as particulate matter originating from emissions of transportation, power plants, and volcanic eruptions, but can also be specifically synthesized to be used in various applications.[78] The methods employed in SPION fabrication can be classified by the governing physical, chemical, or biological processes.[73] Physical approaches involve breaking down large particles into nanometer sizes using bead/ball milling or electron beam lithography methods. Although the top-down approach is suitable for large-scale production, they may not guarantee proper control over particle size and quality.[73,75] In contrast, chemical methods follow a bottom-up approach involving condensation of a material's atoms or molecular entities in solution (i.e., wet chemical method: coprecipitation, sol−gel, microemulsion, hydrothermal, solvothermal, sonochemical, electrochemical, or thermal decomposition) or in gas phase (i.e., flame, laser, or plasma reactors). One of the most conventional techniques for SPION synthesis is coprecipitation of ferrous and ferric ion aqueous salt solutions with a base; however, its applicability is often limited by agglomeration, poor crystallinity, and polydispersity.[79] Recent efforts to overcome these drawbacks include the use of ultrasound, preparation of magnetite nanoparticles under static magnetic field, and use of alkanolamines as base.[80] Recently, thermal decomposition has become a superior method with its promises of high quality, monodisperse SPIONs with controlled sizes and narrow size distribution.[75] However, the need for use of toxic chemicals and additional surface modification to make them water dispersible and biocompatible constitute major drawbacks of this technique.[80] Therefore, the potential of thermal decomposition routes depend on the

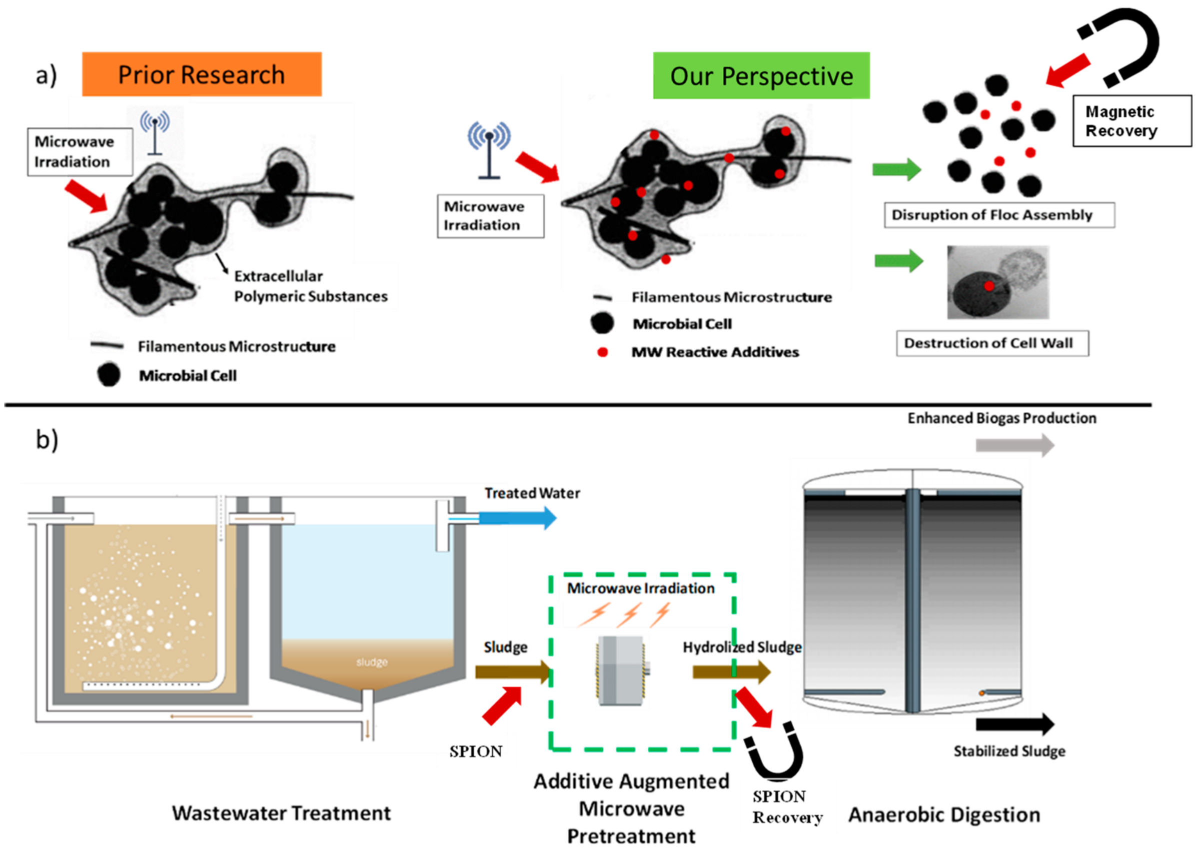

Figure 3. (a) Conceptual depiction of prior research and our perspective. (b) Schematics of integrating MW pretreatment in an existing wastewater treatment plant. Green dashed area shows the suggested location of the SPION-augmented pretreatment process. Figure is adopted from Bozkurt et al.[38]

chemical nature of the iron precursor and surfactant, iron precursor-to-surfactant ratio, reaction time, and reaction temperature (energy inputs).[73] Lastly, biological methods connect nanotechnology with microbial biotechnology either based on using microorganisms to reduce the soluble iron source to nanoparticles or using leave extracts as precipitating agent.[73] Although biosynthetic methods promote greener reactants and products that show good biocompatibility, obtained yields are lower and particle size distributions are broad.[80] While most studies focus on spherical SPIONs, nonspherical iron oxide nanocrystals have recently gained attention with their potential for improving magnetic properties and surface reactivities.[81] Synthesizing nonspherical shapes can introduce unique edges and corners that could significantly change the properties and functionalities of SPIONs.

SPIONs are susceptible to oxidation, agglomeration, and lack of affinity for biomolecules without appropriate surface coating/modification.[73,79] Thus, it is important to understand the role of their surface coating on waste-activated sludge MW prehydrolysis applications. The reason for agglomeration is attributed to high surface area, van der Waals forces of attraction, and dipole−dipole interactions between the particles.[73] To stabilize SPIONs in biological environments, the surface of SPIONs are typically modified with a biocompatible coating either during or after their production.[78] For this, polymers, fatty acids, amino acids, metals, and metal oxides were used to coat SPIONs. Today, polymers are the most popular coating materials, and specifically, poly(ethylene glycol) (PEG) and dextran are the most extensively used ones in biomedical applications due to their high biocompatibility. Polymer molecular weight and surface (grafting) density have shown to be critical with regard to dispersion stability, cytotoxicity, and blood circulation time of SPIONs.[80] Understanding the coating stability in sludge prehydrolysis application would require research to advance the technology from its very early stages.

Upon their tailored synthesis, well-dispersed SPIONs in slurry can efficiently convert MW energy into heat and onto cell walls and floc structures, which will increase energy efficiency of prehydrolysis. In addition, SPIONs can be recovered from slurry without losing physicochemical integrity prior to AD owing to their favorably high magnetic moment and negligible magnetic hysteresis. An effective and quick separation of SPIONs requires an external magnetic field exceeding the Brownian force with higher field strengths necessary as the particle size decreases. For example, homogeneously dispersed 12 nm diameter nanocrystalline magnetite particles were completely removed from a water sample at a very low field gradient of 0.2 T within several minutes.[82] However, the low gradient magnetic separation of smaller-sized SPIONs is often challenging, as magnetophoretic motion is impeded by thermal energy and viscous drag. Recently, magnetically facilitated sedimentation of 5−30 nm SPIONs was achieved in less than 1 h using a quadrupole magnet sorter under horizontal fields and gradients. SPIONs suspended in chloroform/toluene have been recovered at a rate of 93% within 1 h via dipole−dipole interactions, magnetic/gravitational forces, and particle self-assembly.[83] The same setup achieved process equilibrium in 20 min for 5 nm SPIONs suspended in chloroform/toluene.[84] Despite the prominent results obtained in the SPIONs' recovery from low-viscosity media, the literature lacks information on sewage sludge, which is a complex semisolid media expected to obstruct the recovery. However, the proposed prehydrolysis process is anticipated to substantially decrease the viscosity of the sludge by disrupting the sludge flocs and thus yield facilitated SPIONs recovery over untreated sludge. In this context, uniform and well-characterized materials should be synthesized, and their dielectric heating ability to augment prehydrolysis of waste-activated sludge prior to anaerobic digestion should be tested. This involves evaluation of synthesized SPIONs' coordination chemistry, iron core/oxygen shell ratio, particle size, uniformity, and bilayer encapsulation and delineating the role of surface coatings vs the SPION properties on dispersion/suspension, MW reactivity, and magnetic properties. In addition, the stability of the magnetic properties and material integrity should be tested by recovering and reusing the same SPION batches under repeated MW heating experiments.

3. SPIONS' POTENTIAL AS MICROWAVE ABSORBERS FOR SLUDGE PREHYDROLYSIS

Developing a holistic prehydrolysis technology for municipal wastewater treatment facilities that can address cleaner energy needs via augmented biogas production in anaerobic digesters can instigate a fundamental paradigm shift on widely accepted AD process (Figure 3). In addition, developing suspended and recoverable SPIONs presents fundamental and practical transformation potential for nanotechnology-enabled water and wastewater industries. However, it should be noted that there is a need for technology maturation to deploy SPIONs to the field. Furthermore, prehydrolysis minimizes generation of excess digestate, which decreases the transportation and disposal-related footprint of wastewater treatment operations. The application of SPION-enabled pretreatment can also benefit agricultural and industrial wastes, including manure, septic sludge, and cellulose-based pulp slurries.

Figure 3(a) conceptually depicts the conventional MW pretreatment process[9,85,86] and our perspective, which integrates SPIONs to MW pretreatment. Figure 3(b) illustrates the design that we suggest for the SPION-augmented MW pretreatment process in an existing WWTP. The green dashed area highlights the unit operation where SPION-augmented MW pretreatment and magnetic separation processes are carried out subsequently. The design can consist of two cascading tanks, one for pretreatment and the other for magnetic separation process, or a single tank containing two processes operated in batch mode, based on the land availability, capital costs, and operational rewards, and penalties. This novel application requires delicate SPION synthesis to ensure that the SPIONs' properties are preserved during and after MW irradiation.

4. FUNDAMENTALS OF SPION-ENABLED MICROWAVE PREHYDROLYSIS OF WASTE-ACTIVATED SLUDGE

MWs are nonionizing electromagnetic waves with frequencies between 0.3 and 300 GHz. MW heating is achieved by passing an electromagnetic field, typically at a frequency of 2.45 GHz. The interactions between the incident electromagnetic wave and the sludge content dissipate energy in the form of heat depending on sludge properties and irradiation conditions. According to the Stefan−Boltzmann law and Kirchhoff's law, the temperature increase in MW heating follows a nonlinear pattern with the input power and depends on the material's properties. Coupling of SPIONs with sludge may alter the MW absorption rate of sludge and, hence, the heating rate. Given that SPIONs are MW-absorbing materials, the amount of MW available for absorption by the sludge content may decrease. However, SPIONs enhance the transduction of MW energy to heat and therefore lead to an overall temperature increase.[87] Furthermore, SPIONs coupled with MWs can enhance the friction between the particles and sludge cells. An increase in SPION concentration can facilitate the MW absorption rates.[88] Therefore, it is critical to investigate the MW heating interactions of systematically synthesized and well-characterized SPIONs for efficient prehydrolysis applications.

MW prehydrolysis has been studied extensively in the literature (Figure 4).[39,89,90] The literature analysis indicated that MW prehydrolysis is effective converting MWs into heat owing to their favorable dielectric properties and ability to directly interact with the incidental electric and magnetic radiation (more effective than conventional MW absorbers such as silicon carbide, SiC, and other iron oxide crystals such as hematite and maghemite).[91−94] In addition, approximately 75 articles were published in the past 15 years exploring the effect of MW hydrolysis on excess wastewater sludge. These studies report successful MW hydrolysis on secondary sludge (77% of all articles) as a function of specific energy input, as summarized in Figure 4. The MW energy is speculated to disturb flocs and liberate bound organic matter into solution and disintegrate cell walls that are within the EPS shielding microfloc assemblies and release organic matter[95] via three possible pathways: (i) thermal,[23] (ii) athermal,[23,96] and (iii) catalytic oxidation.[97] The thermal effects cover dissolution of organic matter such as denaturation of membrane proteins and release of intracellular organelles[98] and exceeding the boiling point of intracellular liquor (possibly causing breakage of cell walls).[23] High temperatures can also decrease solubility of gases and enable formation of gas domains (bubbles) in the slurry and cause additional stress for cell walls by pressure release if they interact with the cells.[99] On the other hand, elevated temperatures (70−180 °C) were reported to cause low-molecular-weight sugars and amino acids to polymerize

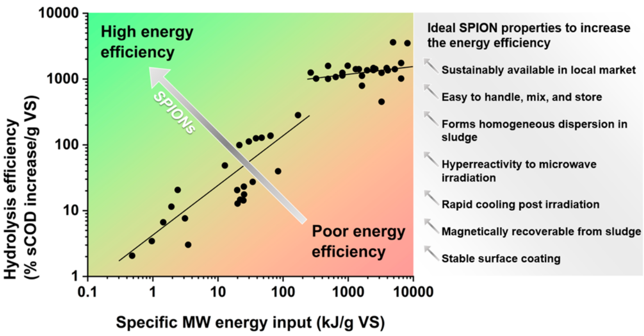

Figure 4. Demonstration for hydrolysis of waste-activated sludge in terms of percent soluble chemical oxygen demand increase in slurry after MW heating as a function of MW energy input. The trendlines indicate typical energy input vs hydrolysis observations. The gray arrow reaching the green region demonstrates that energy efficiency can be achieved with the help of the ideal SPION properties listed on the right. Figure is adopted from Bozkurt et al.[30]

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and form recalcitrant polymer-like organic compounds via Maillard reactions potentially deteriorating the performance of AD.[11,95,96,100−103] Nonthermal MW effects or direct MW interactions are caused by polar and polarizable molecules rapidly oscillating under the incoming electromagnetic waves. The MW energy is converted to heat by internal resistance to rotation,[25,42,104] possibly triggering bond decomposition.[23,96] Nonthermal MW decomposition pathways are speculative in the literature,[18] and these effects are still unknown. Isolating the nonthermal effects experimentally is challenging as differentiating the cause of heating during MW treatment is not a straightforward test. Finally, the ROS at the MW hot spots can degrade cell walls and floc assemblies.[105] The extremely short lifetime reactive species make their experimental investigation challenging in complex sludge matrices. There are studies investigating the hydroxyl radical formation during MW prehydrolysis with some chemical oxidants;[106] however, there are no reports on the catalytic oxidation pathway of WAS using MW irradiation alone. Use of SPIONs in sludge pretreatment is anticipated to contribute to thermal and catalytic oxidation by creating hot spots in slurry with resultant radical formation, but further research is needed to make conclusive remarks about their formation mechanisms. Furthermore, as in many pretreatment applications, SPION-augmented MW prehydrolysis holds the potential to increase the dewaterability of sludge through EPS disruption. The inclusion of SPIONs can potentially enhance the impact by inducing physical disruption of cells in addition to thermal, athermal, and catalytic mechanisms.

5. ENVIRONMENTAL AND ENGINEERING IMPLICATIONS

AD is a well-established, energy-positive sludge stabilization technique; however, its application is often limited by the slow hydrolysis of sludge. MW pretreatment has been applied as a viable approach, providing selective and rapid heating to cell walls and increasing sludge solubilization. Further augmentation of this technique can be achieved by the integration of recent nanotechnology-based advancements. SPIONs spiked into WAS during MW pretreatment can interact (partition) with cell walls while efficiently converting MW energy into local hot spots, which thermally hydrolyzes sludge. The efforts aiming to increase the efficiency of the AD process via SPION-augmented MW pretreatment hold promise for decreasing the transportation and disposal of related footprints of WWTPs. Nevertheless, the improper synthesis, operation, and recovery of SPIONs may raise environmental and engineering concerns. First and foremost, ensuring the high recovery efficiency of SPIONs from pretreated WAS constitutes the backbone of environmental safety. Failure in recovery can cause SPIONs to proceed to the digester and then to the environment through disposal and/or beneficial use of digested sludge. Additionally, improperly synthesized or coated SPIONs may accumulate toxic compounds on their surfaces during retention in sludge and transfer them into the environment unless being recovered.

Further augmentation of the pretreatment process should not interfere with the healthy operation of AD. MW pretreatment typically yields a 2%−170% increase in sludge solubilization by specific energy input up to 100 kJ/g of VS. In more extreme cases, where higher energy inputs of 265−8135 kJ/g of VS are utilized, the solubilization impact can even reach a 1000% to 2000% increase.[38] However, achieving greater solubilization does not always translate to improved anaerobic digestion efficiency.[107] Excessive solubilization can lead to the accumulation of ammonia resulting from the breakdown of proteins, and the toxicity level of ammonia is heavily influenced by the pH levels. Process instability due to ammonia can result in the accumulation of VFAs, which further decreases the pH. This decline in pH levels eventually leads to a decrease in the concentration of free ammonia. The intricate interaction between free ammonia, VFAs, and pH can create an inhibited steady state, characterized by stable process conditions but a lower methane yield.[108] Considering the temperature increase expected from the interaction of SPIONs with the applied MW and the associated effect on the protein, a thorough understanding of the change in sludge composition is needed.

The design for SPION-augmented MW pretreatment must be carefully informed by considering engineering dimensions from the SPIONs' synthesis to tank design. SPION synthesis requires tuning of multiple characteristics including hydrophobicity, magnetic properties, and heat holding capacity for optimized performance. First, selected surface coatings should provide SPIONs stability for homogeneous dispersions, while allowing for close interaction(s) with sludge cells. Second, a high recovery rate is also required to manage technology cost and implications. This is critical as SPIONs may affect AD efficiency, decreasing biogas quantity and quality. Furthermore, consideration for background magnetic metals (e.g., iron, nickel, cobalt) in sludge is necessary, as unintentionally collected/concentrated materials during magnetic separation may decrease the efficiency of the recycling process. Lastly, as SPIONs may lose their ability to magnetize at high temperatures (i.e., Curie temperature), materials also need to be capable of cooling relatively quickly. The discussion in this perspective intends to highlight the constraints of SPIONs so that precise engineering approaches can be developed to overcome them.

Realization of this technology also requires performing extensive feasibility studies, starting from filling out the essential information in the conceptual model presented in this perspective to obtain a cost−benefit analysis. Moreover, a meticulous investigation of sludge constituents, including the microbial consortium, is essential to gain profound insights into the reaction mechanisms initiated by SPIONs under microwave radiation and their subsequent impact on the AD process. A thorough understanding of the mechanisms can guide us in maximizing the potential of nanotechnology not only to enhance the methane yield but also to improve the quality of the produced biosolids for further handling. Furthermore, performing optimization studies for the recovery of SPIONs from the reactor is integral to this technology, as it reduces costs and prevents the release of nanoparticles into the environment. Achieving this goal necessitates collaboration between environmental and material scientists, and this can stimulate further research questions and expand the application scope of the technology.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.3c00673.

Conceptual model for techno-economic assessment of the proposed technology (Text S1) and comparison of the proposed technology with conventional techniques (Text S2). Lists and semiquantitative comparison of conventional sludge pretreatment techniques with the proposed technology (Table S1) (PDF)

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Notes

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