

Review

Efficacy Studies of Silica Nanoparticles Synthesized Using Agricultural Waste for Mitigating Waterborne Contaminants

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Abstract: In recent years, there has been a steady increase in the quantity of agricultural waste generation, due to the increased production of the food supply chain and the production of fuel for greenhouse gas (GHG) emission reduction initiatives, viz. processing, and consumption. As a result, there have been a number of environmental concerns, such as waste disposal, governance, and environmental impact. Hence, repurposing such wastes into high-value goods such as silica nanoparticles (SNPs) has received a lot of scientific attention. Because of their controllable pore size, large surface areas, and tunable and tailorable structure, SNPs have attracted interest from scientists for a variety of applications. As the water resources are becoming scarce and heavily stressed, our ongoing efforts have been towards the green synthesis of nanoparticles, with an emphasis on mitigating waterborne contaminants. Recent advances in the synthesis of SNPs from barley and rice husk agricultural waste, as well as its use in the removal of several recent environmental pollutants from water, have attracted the attention of several researchers, including our group. By fine-tuning the processing parameters during synthesis, the characteristics of SNPs are altered in terms of their configuration, appearance, porosity, and dimensions. Such features and corresponding applications of the SNPs are being investigated in order to investigate whether agricultural waste may be utilized for silica precursors. Although the utilization of low-cost waste-derived minerals appears to have the potential for both waste reduction and the creation of value-added goods, further studies are needed to increase silica production, particularly on a commercial scale. In addition, we conducted a review of the efficacy of SNPs toward water contamination mitigation and our results of such investigation are reported here. It is observed that silica nanoparticles can be synthesized on a commercial scale using green chemistry principles and are highly efficient materials with promising outcomes for environmental applications. Hence, using green synthesis, we are able to reduce agricultural waste, while mitigating environmental contaminants using environmentally friendly processing.

Keywords: agricultural waste; adsorption; nano-silica; wastewater; petroleum contamination



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1. Introduction

Silica, also known as silicon dioxide (SiO₂), has a number of unique features, including varying and tunable pore size, customizable interface, superior mechanical qualities, and chemical makeup that is relatively benign chemically, making it an ideal material for a variety of applications [1]. Due to its non-toxic and biocompatible characteristics, it has been widely employed in the food and medical industries [2]. Furthermore, due, in part, to its occasionally hydrophobic qualities, silica is used as an ingredient in commercial epoxy resin and coating materials [3]. SiO₂ nanoparticles can be mesoporous and depending on the synthesis procedure they may or may not have pores [4]. Mesoporous silica nanoparticles

(MSNPs) of various types, including MCM-41 (Mobil Composition of Matter #41) and SBA-15 (Sigma Aldrich mesoporous <150 μm particle size, pore size 4 nm, hexagonal pore morphology material), have been synthesized with a variety of pore geometries and particle morphologies. Silica nanoparticles typically have a large specific surface area, a high porosity, chemical inertness, and a diverse set of surface functional groups [5]. These distinguishing characteristics enable them to be custom tailored for a variety of applications, including adsorbents, catalytic supports, sensing materials, polymer reinforcement, and advanced composites [6–8]. Although silica can be found in practically every mineral on this planet, the traditional technique of synthesizing nano-silica typically requires a high-temperature process, which makes the resulting nanoparticles energy and cost-intensive.

To manufacture chemical precursors, the traditional approach initiates the extraction of silica from a silica source, such as quartz sand. These precursors are subsequently utilized to prepare SiO_2 . Due to the significant quantity of carbon dioxide (CO_2) generated during the extraction process [9], this traditional approach may contribute to GHGs, commonly attributed to climate change. The Stöber process is a chemical process, in which sodium carbonate (Na_2CO_3) powder is burned with quartz sand at roughly 1300 $^\circ\text{C}$ to generate silicate sodium (Na_2SiO_3) powder before reacting it with sulfuric acid (H_2SO_4), which is the most prevalent method used to synthesize SiO_2 . To make one ton of SiO_2 , 0.53 tons of sodium carbonate (Na_2CO_3) and 0.51 tons of H_2SO_4 are typically utilized. This produces 0.23 tons of CO_2 , 0.74 tons of sodium sulfate (Na_2SO_4), and 20 tons of effluents, all of which contribute to the environmental impact [10] in terms of emissions and effluents. To produce SiO_2 nanoparticles on a commercial scale, a more ecologically friendly, green, and cost-effective technique is required. Furthermore, repurposing agricultural and industrial waste is a critical technique for achieving long-term environmental sustainability [11]. The production of nanomaterials using agricultural, industrial, and residential waste is seen as a viable method of waste treatment and recycling. This is consistent with local, state, and even federal initiatives, such as waste-to-wealth, minimal waste creation, and green chemistry [12,13]. Rice husk [6,14], sugarcane bagasse [15], and palm kernel shells are some of the typical examples of wastes that may be appropriated for SiO_2 production [11,16]. Due to its high silica concentration, agricultural waste is deemed a viable raw material for the commercial production of SiO_2 . Crop residues including grain chaff, sugar molasses, and coconut hulls are progressively being employed in the biosynthesis of nanoparticles, particularly for silica because they are cost-effective regenerative sources with significant silica content. The utilization of waste, particularly agricultural waste, for the manufacture of silica, using green synthesis, is highlighted in this investigation, due to its significant environmental benefit. Furthermore, the impact of chemical treatment on the characteristics of synthesized MSNPs is investigated along with the features and uses of silica nanoparticles in water pollution and contamination mitigation.

Water pollution and waste creation are two major environmental concerns that occur on a regular basis in today's society. Being a natural consequence of the use of technologies, the mitigation of contaminants in water and ways to use waste for creating something useful has recently attracted the attention of several researchers [17–20]. Since water is a fundamental requirement for sustaining the life of all living species, the ever-increasing demand for water, global water scarcity, and water stress present a major concern for society, scientists, and policymakers. Water stress and scarcity reduce the quantity and quality of water (termed as water quality index, WQI) accessible to them [21]. The constant discharge of harmful chemical compounds into water sources is a result of industrialization and population growth [11,16]. According to various studies on water pollution, there are a variety of pollutants that contaminate water's integrity, and among these pollutants are heavy metals (HMs) [22] and oily substances [23] that have been identified as major pollution contributors. Such contaminants have toxic effects on both biotic and abiotic parts of the environment, and they require special attention due to their highly poisonous impact on humans and the environment [19,20]. HMs are refractory pollutants that are generally found in both waste and treated water, and their prevalence is rising on a daily

basis as a result of the increased usage of heavy metals in the industry [22]. HMs are also known to be extremely harmful due to their poisonous and carcinogenic properties, as well as the fact that they are persistent and non-biodegradable, and hence accumulate in the environment for lengthy periods of time [23]. Cadmium, lead, nickel, chromium, and zinc are some of the hazardous elements [19,20]. Due to the occurrence of these heavy metals in water, a variety of treatment techniques for removing them from polluted water have been developed and reported in the literature. However, one of the main drawbacks has been that such contamination mitigation techniques are expensive, generate a considerable quantity of sludge that must be disposed of, or are ineffective under certain conditions. The adsorption approach is one of the ways that has proved to be effective, yet it should be noted that the performance of an adsorption process is dependent on the adsorbent [19,20]. It is well known that exploration, extraction, storage, and distribution of oil and petroleum products are all prone to leakage, which causes significant environmental harm. The incidences of pollution of groundwater and surface water by petroleum products have recently increased, which is evident by the presence in water sources. This has had an impact on water quality all around the world, particularly in areas where petroleum products are produced, transported, and used at significant rates. There have been further instances of long-chain hydrocarbon contamination in both ground and surface water [21]. Water pollution caused by petroleum products is becoming a major public health hazard since it puts humans, plants, and animals in danger [24]. The cost of extracting petroleum from surface water and keeping it from polluting the coastline is high, and it necessitates the deployment of high-tech equipment and specialized chemicals. As is evident from several cases, such as Exxon Valdez, Deepwater horizon, and many other accidents due to petroleum pollution, considerable environmental and economic losses have been caused, while the petroleum product may not be recoverable after contamination. As a result, researchers must develop low-cost technologies for treating petroleum-contaminated water. For years, several environmental scientists, engineers, and research groups have conducted extensive research on water contamination caused by petroleum products, resulting in several solutions, each of which has contributed to minimizing the amount of harm to water and the environment. However, the primary aim has been to reduce petroleum pollution, and not eliminate, and harm to the water body and aquatic life; as a result, the remedial reaction must be conducted quickly.

There have been various studies on nanoparticles as adsorbents, and the majority of them have shown that adsorbents in their nano-dimensions form are more effective and efficient, which may be related to nanoparticles' capacity to target specific contaminants. Membrane filtration, redox processes, ion exchange, and adsorption are some of the most common processes used by scientists to remove heavy metals from wastewater [25,26]. Adsorption is considered a highly distinctive process for successful wastewater treatment procedures and adsorbents are created using synthesis methods, such as from agricultural waste. One of the qualities of a green adsorbent is that it must be cost-effective, have considerable adsorption capabilities, and must be reusable. This review discusses our investigation of the environmentally friendly synthesis of SNPs utilizing a naturally accessible agricultural waste material (barley and rice husk) as green adsorbents for removing petroleum products and HMs from contaminated water.

1.1. Silica Nanoparticles

Despite the ubiquitous presence of silica in the earth's crust, it is commercially produced using synthesis processes that use a variety of sources, including agricultural wastes [27]. The resulting SNPs are used for several industrial applications, ranging from electronic components to targeted drug delivery. As per recent trends, a market share of goods consisting of silica nanoparticles was estimated at around USD 8.8 billion in 2020 [28], showing significant future market trends. Silicon (Si), as one of the elements in silica, is normally available in crystalline, polycrystalline, or amorphous form, and it is available as silicon dioxide (SiO₂) and is commonly used for various applications in

industry, including the applications, such as plant development to eliminate biotic and abiotic stresses [29]. Overall, silica is produced using chemical sources such as tetramethyl orthosilicate (TEOS) or sodium silicate; however, since silica naturally occurs in sand, flint, or quartz in various forms, it requires a lot of energy to complete the synthesis process, which is usually quite complicated. It should also be noted that high energy consumption and temperature requirements for manufacturing are often exceedingly expensive, unsustainable, and ecologically unfriendly. As a result of this concern, several researchers are working on ways to develop new processes for producing silica nanoparticles that are simpler, less expensive, and more ecologically friendly using principles of green chemistry [13]. Quite independently, the production of solid waste poses a huge environmental concern, especially as the landfills are filling up rapidly with associated GHG issues, including the release of solid waste in aquatic environments. Hence, it is critical to find new ways to minimize the quantity of solid waste. Agricultural waste, or solid waste derived from agricultural goods, is an important contender for producing silica nanoparticles. Rice, corn, barley, wheat, sugarcane, and other agricultural crops create solid waste on Earth; thus, the amount of solid waste left on the ground should be decreased by using them as an alternate source for producing other critical resources. Several products with high silicon content are utilized to make silica nanoparticles, which in turn are also employed to solve an environmental problem since they are waste products that have been turned into valuable resources. Since converting wastewater into a usable water resource has become an area of great interest to many researchers, we have ventured into using rice husk, wheat straw, barley grass, and other agricultural wastes utilized as sources to make silica nanoparticles [19,20,30,31].

1.2. Processes in the Synthesis of Silica Nano-Particles

To process agriculture waste products into SNPs consisting of specific forms, sizes, dimensions, nature, and structures, several processing methods are used and are generally categorized as top-down (physical strategy) or the bottom-up (chemical approach), as two commonly used methods for producing silica particles. The top-down strategy is characterized by the use of externally controlled tools or processes that are used to cut, mill, and shape materials into the desired shapes and sizes. Conversely, the bottom-up technique, a preferred strategy for creating SNPs, consists of processes in which molecular components arrange themselves into more complex assemblies via atom-by-atom, molecule-by-molecule, or cluster-by-cluster approaches [32]. The main driving force behind the bottom-up approach is the reduction in Gibbs free energy, ΔG , and the materials thus produced are close to their equilibrium state. An approach where both of these techniques are employed is known as a hybrid approach, such as lithography.

The top-down or physical method is characterized by employing unique size reduction techniques to reduce the dimension of the original size [33]. These methods depend on bulk material removal, etching, or division, as well as bulk process downsizing, i.e., to produce the necessary attrition framework attributes [34]. The milling process is an example of a top-down strategy, in which bulk materials are broken down to achieve small particles [35]. Ball milling is a shear-force-dominating process that uses impact and attrition to decrease particle size. It employs a revolving shell to generate centrifugal force and metallic balls (typically Zirconia or steel balls) as the grinding medium [36]. This method is generally extremely cost-effective, with good product purity, low-temperature reaction, controllability, convenience, and repeatability [37]. However, due to the production of structural faults in the generated material, the top-down synthesis approach requires additional modification. This is a serious constraint since the material structure substantially influences the surface chemistry and other physical properties of nanoparticles. Furthermore, the resulting material may have a high level of “dust” from flying particles. Despite these major disadvantages, this approach is thought to be suitable for large-scale production since it allows for deposition across a vast substrate and does not require chemical purification [38].

Chemical aggregation of SNPs via atom-to-atom or molecule-to-molecule processes is part of the bottom-up strategy [39]. Since it provides an exact particle size control, this approach is preferred for nanoparticle elaboration. Furthermore, bottom-up procedures are more adaptable and are based on the self-assembly principle, thus, this strategy has resulted in a wide range of nanoparticle production methods [38]. The high yield purity of this approach has considerable benefits [40]. Chemical vapor deposition (CVD) is a method for condensing vapor-phase chemicals into solid-phase materials [41], generally for greater resistance, erosion protection, and a combination of the two used for many applications [42]. CVD is widely used for producing large-scale and high-purity fused silica glass [43]. In order to synthesize SiO_2 , a precursor is injected into an H_2/O_2 flame. The subsequent steps include chemical transformation from precursor to oxide, the nucleation of oxide vapors, the collisions of oxide particles, the condensation of oxide vapor onto oxide particles, and the sintering of oxide particles. However, it is not easy to control the concentration of each precursor during the synthesis of multi-component particles. Halide compounds, such as silicon tetrachloride (SiCl_4), are commonly used as a starter for the CVD production of silica glass in the industry. However, this approach necessitates high temperatures and has a slower rate of development. It also uses potentially toxic reagents including SiCl_4 , nickel tetracarbonyl ($\text{Ni}(\text{CO})_4$), and diborane (B_2H_6). Some of these reagents are explosive and caustic in nature [44]. Hydrothermal synthesis, in conjunction with CVD, is yet another method used to produce silica. Hydrothermal procedures are often carried out in a high-pressure confined compartment using subcritical or supercritical solvents [45]. Traditional hydrothermal methods have a number of limitations, including low yield, long process times, as well as heterogeneous structure. This problem can be fixed by using a regular microwave [46], which provides precise control of the shape of the resultant nanoparticles [47], as well as the production of materials that are unstable at the melting point and yet produce large, high-quality crystals [48]. It does, however, necessitate the use of a high-temperature furnace and substrate holder, as described by Narayan et al. [4]. Using similar chemicals, this approach may regulate the size, shape, and crystal structure of metallic nanoparticles, resulting in a sequence of seeds of varying shapes and sizes.

Controlling reaction length, temperature, and reaction conditions will also provide a variety of geometries that might be useful in a variety of study domains [49]. Furthermore, this approach necessitates a substantial quantity of surfactant, and the stability of the microemulsion is impacted by the pH [48]. One of the earliest strategies for creating engineered nanomaterials was sonochemical synthesis [50]. Ultrasound irradiation is a straightforward method for producing a variety of nanomaterials from inorganic precursors, most often via primary, secondary, or combination methods (sonochemistry effects). Primary sonochemical synthesis refers to the intense transitory conditions such as high pressure and temperature from the collapse of the cavitation bubbles, whereas secondary sonochemical synthesis exploits the post-produced chemical repercussions in the liquid phase. As a result, this high-intensity ultrasonic method for nanoparticle synthesis eliminates the requirement for bulk high temperatures, high pressures, or long reaction times [47]. However, this approach yields a low number of materials [38]. Chemical precipitation is a popular approach for making SNPs since it is energy efficient and has a short processing time [51]. The co-precipitation approach, also known as the solid-state counterpart or a side-branch of the sol-gel process [52], is another successful soft chemical method of mixing oxide materials. Whenever deposition, development, coarsening, and/or agglomeration processes all occur simultaneously, it is termed a co-precipitation response. This process is straightforward, allows for precise size and depositing control, uses minimum heat, and hence is energy efficient [53]. It also has the advantage of immediately creating homogeneous nanomaterials with tiny sizes and dispersion into the solution via various chemical processes [54]. However, according to Rane et al. [53], this method is not suitable for uncharged species, and the product produced may contain precipitated trace contaminants. It also has problems with batch-to-batch repeatability. Finally, the sol-gel approach has been widely used to create MSNPs because of its capacity to produce a pure

and homogeneous product under moderate conditions [39]. It is a straightforward, cost-effective, and efficient production technique [38], however, the method utilizes expensive raw materials, as well as uses a high-temperature furnace [44]. This process involves the hydrolysis and condensation of metal alkoxides, such as tetraethyl orthosilicate, formally named tetraethoxysilane (TEOS) ($\text{Si}(\text{OEt})_4$), or inorganic salts such as sodium silicate (Na_2SiO_3) in the presence of an acid or base [4,39]. Temperature, water content, pH, surfactant, or copolymer characteristics, and the amounts and sources of silica used in the process all impact the dimensions and morphologies of the final products [5].

2. Materials and Methods—Pre-Preparation of Agricultural Waste Material

According to recent studies [19,20,27,30,34], converting agricultural waste into nano-silica requires a finite preparation. The steps include washing the pre-cut waste samples (barley, wheat, and rice husk waste) using distilled water to remove any adhering sand, soil, and other visible particles from the straws. The resulting sample is normally dried in the oven for 24 h at 100 °C. In fact, the drying process could either be sun drying or oven drying, which is followed by a ball-milling to convert the waste into powder, which is then refluxed in proportionate amounts using 2 M HCl solution for ~6 h each. After the acid reflux, the samples are filtered and washed in distilled water, followed by heating at 700 °C for ~5 h. The resulting samples are, once again, dissolved in 10% HNO_3 for ~3 h and then rinsed with distilled water, filtered, and allowed to cool, during which nano-silica is precipitated. Figure 1 shows a typical schematic diagram of the experimental procedure [30] used for converting barley husk into nano-silica. Heating generally helps in removing any organic contents, while acid reflux helps remove metallic impurities from the barley.

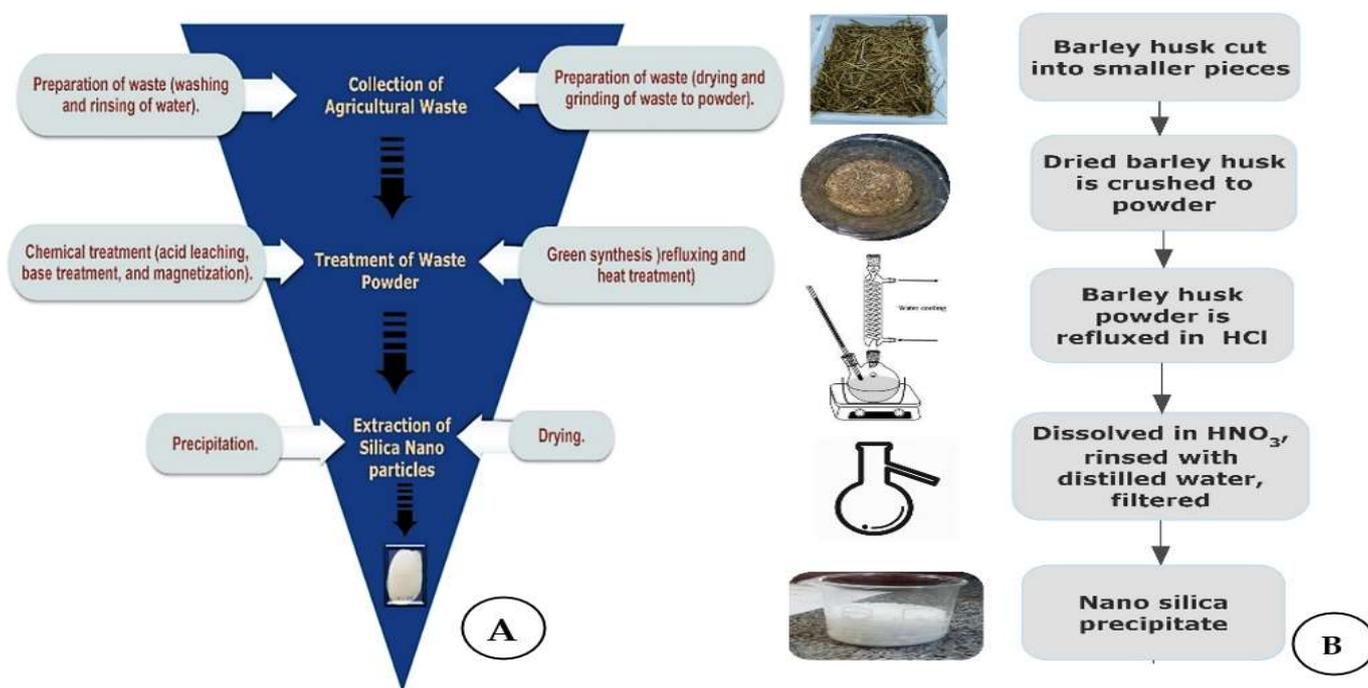


Figure 1. Schematic diagram of the experimental procedure (A): block diagram; and (B) process used. Adapted, in part, with permission from Ref. [30]. 2020, Akhayere et al.

2.1. Preparation of Hydrophobic Nano-Silica and Zeolite

Nano-zeolite is generated by blending freshly produced homogeneous aluminate and silicate solutions. The sodium aluminate solution is typically produced by dissolving 5 g of sodium hydroxide (NaOH) in 50 mL distilled water and then by adding ~1.3 g of sodium aluminate ($\text{AlO}_2\cdot\text{Na}$ or NaAlO_2 or AlNaO_2) at 100 °C. To produce the nano-silica mixture, 1 g of recovered silica was diluted in a 50 mL solution that contains 5 g NaOH. The

aluminate and nano-silicate fluids are then allowed to cool. After cooling, the nano-silicate solution is gradually added to the aluminate solution, which is then continuously stirred to form a clear solution [20,30]. The solution is then heated at 40 °C for 18 h and the samples are then dried overnight at 60 °C.

2.2. Preparation of Magnetic Nano-Silica

To convert nano-silica into magnetic nano-silica (M-NS), it is first necessary to create a magnetic solution, which is then mixed with the nano-silica solution. The magnetic nanoparticles are generally synthesized using iron (III) chloride (FeCl_3) as a precursor. At room temperature (RT), 20 mL of barley leaf extract/powder is gradually introduced into 200 mL of 1 mM FeCl_3 solution. The resulting mixture is agitated for 60 min at ~10,000 rpm using a homogenization stirrer [30,55]. The color of the mixture changes to a very dark brown during this process, suggesting the creation of magnetic nanoparticles. Immediately after that, the mixture is centrifuged two–three times for a 10 min interval each, followed by rinsing twice with alcohol. During this procedure, the color of the combination is darkened steadily. The magnetic behavior of particles becomes readily visible when a magnet is brought in close proximity, as illustrated in Figure 2.

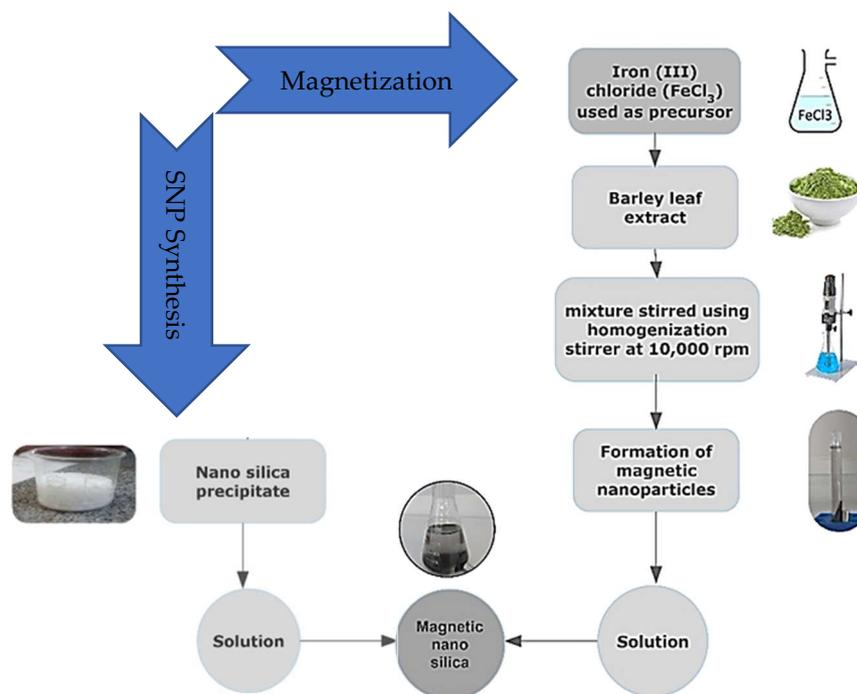


Figure 2. Schematic diagram of the experimental procedure to produce magnetic nano-silica. Adapted, in part, with permission from Ref. [30]. 2020, Akhayere et al.

2.3. Synthesis of Amorphous Nano-Silica

To prepare amorphous nano-silica, a somewhat similar procedure is applied to agricultural waste, such as barley and wheat grass. To remove dirt and other particles, the agricultural wastes are generally rinsed with distilled water and dried for ~24 h at 100 °C. As with other processes, a ball miller is used to grind the material into finely powdered samples of barley and wheat grass. To extract pure SNPs, 50 g of barley and wheat grass powder are processed in a solution of ~250 mL 10% *w/v* HNO_3 , cooled, and then washed with distilled water. The processed samples are then heated in a furnace at ~700 °C for about 5 h after being refluxed with 250 cc of 2 M HCl for 6 h. From 50 g of barley powder, a total of 46.4 g of NSP was recovered, yielding a 92.4% yield. Depending upon the nature of agricultural waste and desired nature of nanoparticles, some of the following steps are used during synthesis.

Pretreatment: Normally the agricultural waste is cut into small pieces, weighed, soaked for about 3 h, and dried at 110 °C overnight. The resultant material is then crushed to 60–80 mesh before being submerged in hydrochloric acid for acid leaching. The material is then washed, filtered, dried, and then stored.

Heat treatment: Roughly 2 g of processed rice husk is weighed and set in a controlled-environment furnace on a flat-bottomed crucible. The processed material is generally heat-treated in an atmosphere of air in a furnace heated to 500–700 °C at a rate of 10 °C/min. Once the desired temperature is attained, the sample is kept in the furnace for 3 h to eliminate organic materials from the pre-treated samples.

Preparation of a Ni/SiO₂ catalyst. The impregnation process is used to make a 10 wt.% Ni/SiO₂ catalyst. After dissolving a specified amount of nickel nitrate in water, the heat-treated sample is added and the suspension is agitated for 2 h before being transferred to a water bath and then dried. The samples are then baked overnight and calcinated for two hours in a muffled furnace heated at about 600 °C.

Acid treatment: Many studies have looked at using industrial waste, notably fly ash (FA), to make SiO₂ nanoparticles [56,57]. Due to the ease of these techniques, chemical pathways are used in the majority of such methods. Acid leaching treatment, alkaline treatment, and silica recovery are the three basic processes involved in chemical treatments. Acid leaching [58] is a useful pre-treatment method for removing organic materials and metallic contaminants from the waste. The output and purity of silica rise greatly while using the acid leaching technique, producing a greater surface area for silica products [59]. This is due to the fact that acid leaching alters the chemical makeup of the waste [59]. Acid-treated waste has a low degree of silica crystallization during the combustion process, according to Kwan and Wong [58]. The waste is less sensitive to the combustion temperature since the crystallization catalyst has been eliminated. In comparison to non-acid-treated waste, the combustion process at a regulated temperature yields acid-treated waste with high amorphous SiO₂ content, low alkali oxides, low unburned carbon, smaller particle size, and large specific surface area.

Alkaline Treatment is a crucial step for breaking up the waste's chemical composition in an alkaline media and hence increasing silica production [60]. Due to its mild acidic nature, silica does not react with water [61], however, strong basic reagents, such as KOH and NaOH, do react with silica. The method of creating Na₂SiO₃ solution from raw materials using a NaOH solution is well known as an alkaline treatment, where numerous factors must be managed, including the concentration, temperature, and duration of the process. The purity, crystallinity, and surface area of the silica product are all affected by such variables. The crystallinity and specific surface area of the particles are affected by the concentration of the alkaline solution, according to Fajaroh et al. [61]. The two Si–O amorphous silica bonds must split the linkages based on bond energy to form the intermediate monomer structure. Quartz, on the other hand, necessitates the dissolution of four Si–O bonds and a single Si–O bond, which is usually accomplished using a high-pressure hydrothermal process. Zhao et al. [62] also observed that the reaction temperature of the alkaline treatment impacted the rate of silica extraction. This is because amorphous silica has a high dissolving capacity. However, the process duration has an effect on silica solubility, which also impacts the purity of silica. Thus, the alkaline content is one critical factor that has a considerable impact on the silica product. The greater the concentration of the silicate solution, the smaller the crystallinity of the particles formed and the larger the specific surface area of the particles generated [61]. Farirai et al. [15] used a 2 M NaOH solution to perform an alkaline treatment on sugarcane bagasse ash. It effectively achieved high purity amorphous silica with a specific surface area of 240 m²/g and a purity of 98.92% with a range from 6 to 24 nm. During the synthesis stage, the alkaline treatment caused particle agglomeration, which resulted in clusters. In comparison to the commercial silica used in this study, the surface area of the synthesized silica was also higher. Zhao et al. [62] also examined the silica extraction rate of five different concentrations of NaOH solution employed during the alkaline treatment (1, 2, 3, 4, and 5 M). The silica extraction rate

rose from zero to 85.66% when the concentration of the NaOH solution was raised from 0 to 5 M. The amount of NaOH in the solution had a large influence on silica extraction. The silica recovered was mostly in the form of amorphous silica, which was obvious. Concurrently, Sethy et al. [63] produced Na_2SiO_3 from bamboo leaf ash using a 1 M NaOH solution. Along with a few large-sized agglomerated nanoparticles, a high percentage of amorphous silica nanoparticles with an average particle size of 20 nm were produced. Fatimah et al. [64] employed a 4 M NaOH solution in an alkaline treatment procedure to extract silica from bamboo leaf ash. Amorphous biogenic silica with a purity of 96.4% and a surface area of $98 \text{ m}^2/\text{g}$ was successfully produced, with no impurities found [65]. It is vital to think about how reaction temperature affects silica extraction, especially in terms of yield, purity, crystallinity, and surface area of the silica product. Park et al. [66] investigated the effectiveness of silica extraction at six different alkaline reaction temperatures (25, 60, 70, 80, 90, and 100 °C) and discovered that only a small quantity (1.4–14%) of silica leached from the rice husk into the NaOH solution at 25 °C. At 60 °C, the silica output increased to 68.4%. The silica production, however, did not improve after reaching 70 °C. The optimal reaction temperature for the alkaline solution of rice husk was found to be 70 °C. As a consequence, 98.5% pure amorphous silica with a surface area of $1.97 \text{ m}^2/\text{g}$ was effectively produced.

3. Characterization of Synthesized Silica Nanoparticles

Several techniques are used for the characterization of SNPs to assess their chemical composition, morphology, porosity, and other relevant indicators. We characterized SNPs using X-ray fluorescence (XRF) and the results indicate the presence of SiO_2 as the highest compound present in the samples, with the percentage ranging from 96% to 93%, as produced from sources. Other compounds such as K_2O , SO_3 , CaO , Fe_2O_3 , CuO , and ZnO were also present in trace amounts. XRD characterization also displayed broad diffraction peaks between 30 and 32, which are mainly associated with amorphous structures, showing the formation of SNPs in their amorphous state. Figure 3A,B show results of nano-silica formation from barley husk and barley grass, respectively, while Figure 3C,D show formation from barley wheat grass [19,31]. It should provide a concise and precise description of the experimental results, their interpretation, as well as the experimental conclusions.

We conducted Fourier-Transform Infrared (FTIR) analysis over the range of $400\text{--}4000 \text{ cm}^{-1}$, as shown in Figure 4A,B, where the formation of nano-silica using barley husk and barley grass is evident, while Figure 4C shows the formation of nano-silica resulting from barley wheat grass [19,31]. A large number of FTIR peaks were identified and recorded. This study is critical for determining which other functional groups are present in nanoparticles, since the results show a dominant peak at 1076 , 1060 , and 1800 cm^{-1} for nano-silica from barley wheat and rice husk sources. These peaks are attributed to vibrations that correspond to the asymmetric stretching vibrations of silicon bond (Si-O-Si), other peaks could be seen around 3280 cm^{-1} corresponding to OH bending vibrations.

Particle size assessment was also performed to identify the nanoparticle sizes. In addition, Zeta Sizer and Bruner–Emmett–Teller (BET) were used to study the surface and sizes of the nanoparticles. The particle sizes were seen to be around 70, 102, 145, 131, and 25 nm, for barley grass, wheat, barley husk, and rice husk nano-silica, respectively. Particle size is a critical characteristic because it affects the surface area of nanoparticles; the smaller the particle size, the larger the surface area, and hence the higher the adsorption capacity due to higher surface activation energy.

The amount of aggregation and the surface area of the nanoparticles were also characterized using Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). The SEM images in Figure 5A,B showed very little agglomeration while in Figure 5D,E we observed a growing presence of agglomeration. Energy-dispersive X-ray (EDX) analyses were also conducted to determine the constituent elements and chemical compounds.

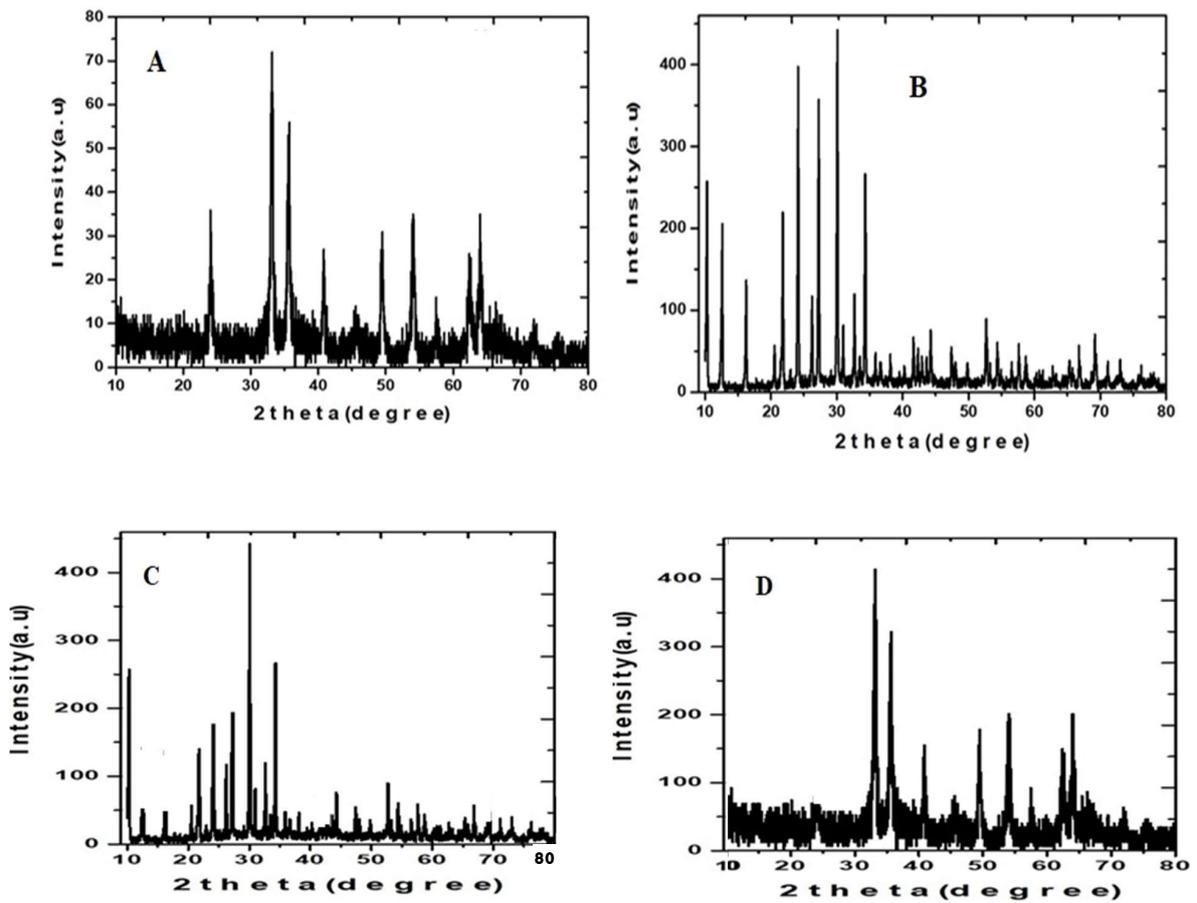


Figure 3. XRD images of synthesized silica nanoparticles for (A) barley husk, (B) barley grass, (C) barley, and (D) wheatgrass.

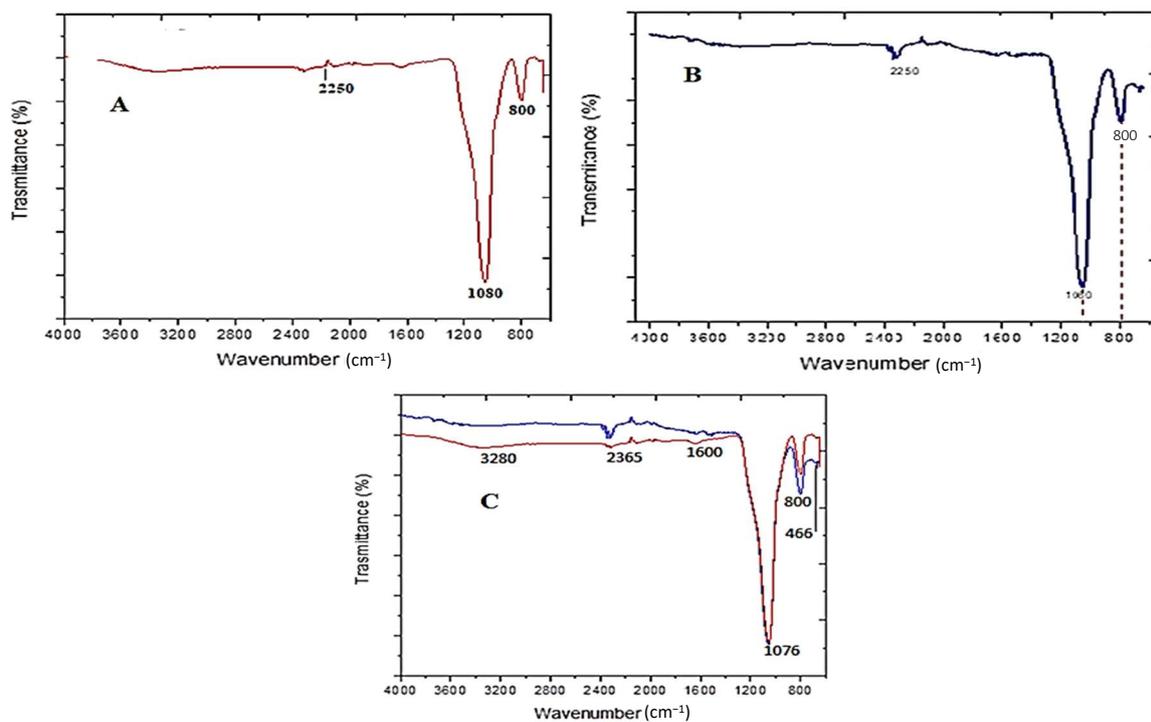


Figure 4. FTIR images of synthesized silica nanoparticles for (A) barley husk, (B) barley grass, (C) and barley and wheat grass.

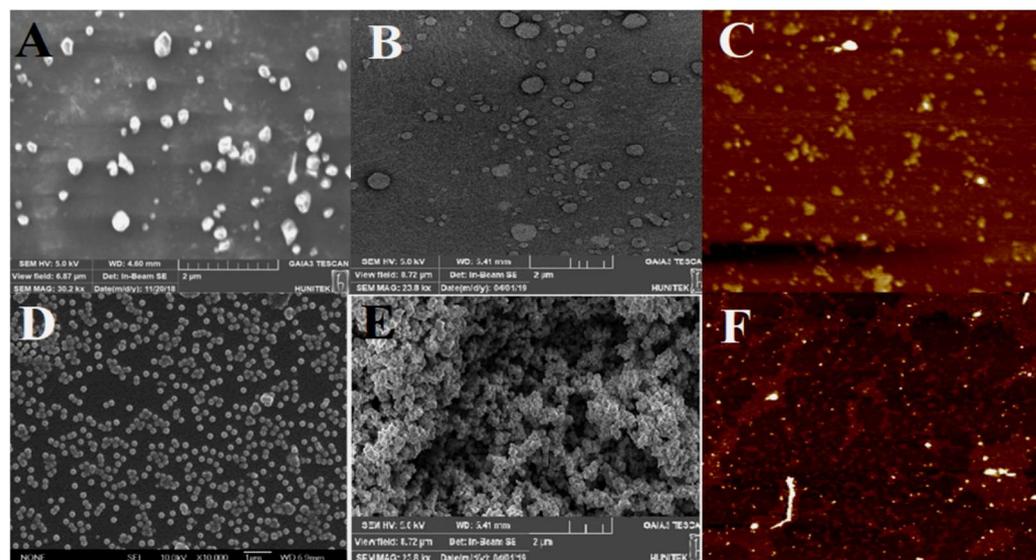


Figure 5. SEM images of synthesized silica nanoparticles for (A) amorphous NS barley; (B) amorphous NS wheat; (C) AFM results for NS barley; (D) magnetic NS barley; (E) hydrophobic NS barley; and (F) AFM results for NS wheat.

According to the acquired data from Table 1, we can see from the EDX results of silica nanoparticles the presence of silicon, as the largest peak, followed by carbon and oxygen. The compound composition of the various precursor sources, according to the results, suggests that barley contains a significant content of silica nanoparticles. Table 1 shows FTIR, XRD, particle size, and EDX results. Since nanoparticles have larger surface areas [67] with higher surface activation energy, they serve as adsorbents for the removal of contaminants in water. It is critical to carry out both X-ray fluorescence (XRF) and EDX characterization techniques since the EDX methodology alone may be inadequate to provide a complete description of the sample.

The XRF analysis provides the emission of characteristic secondary (or fluorescent) X-rays from a material that has been excited with high-energy X-rays or gamma rays, which leads to the elemental analysis and chemical analysis of the specimen under investigation and is a more effective way to identify the chemical components that make up the nanoparticles as constituents. Table 2 provides compositions of SNPs using X-ray fluorescence (XRF) showing the presence of SiO_2 as the highest compound present in the samples, with the percentage ranging from 96% to 93%, while other compounds, such as, K_2O , SO_3 , CaO , Fe_2O_3 , CuO , and ZnO were also present in trace amounts.

Table 1. Characterization results of nanoparticles from different sources.

Silica Nanoparticle	FTIR	XRD	EDX	Particle Size	Reference
Barley-grass-synthesized nano-amorphous silica	Si-O-Si $\sim 1076 \text{ cm}^{-1}$	Amorphous	Si, O, and C	70 nm	[31]
Wheatgrass-synthesized nano-amorphous silica	Si-O-Si $\sim 1076 \text{ cm}^{-1}$	Amorphous	Si, O, and C	102 nm	[31]
Barley-husk-grass-synthesized nano-amorphous silica	Si-O-Si $\sim 1060 \text{ cm}^{-1}$	Amorphous	Si, O, and C	145 nm	[30]
Barley-grass-synthesized nano-amorphous silica	Si-O-Si $\sim 1080 \text{ cm}^{-1}$	Amorphous	Si, O, and C	131 nm	[20]
Rice-husk-synthesized nano-amorphous silica	Si-O-Si $\sim 1080 \text{ cm}^{-1}$	Amorphous	Si, O, and C	25 nm	[68,69]

Table 2. XRF compositions of nanoparticles from different sources.

Compounds	Barley-Grass-Synthesized Nano-Amorphous Silica%	Wheatgrass-Synthesized Nano-Amorphous Silica%	Barley-Husk-Synthesized Nano-Amorphous Silica%	Rice-Husk-Synthesized Nano-Amorphous Silica%
SiO ₂	96.203	93.01	96.30	96.51
K ₂ O	1.510	0.297	1.410	0.297
SO ₃	0.855	0.168	0.855	0.168
CaO	0.797	0.157	0.697	0.157
Fe ₂ O ₃	0.422	0.083	0.322	0.17
Cr ₂ O ₃	0.067	0.013	0.067	0.013
MnO	0.058	0.011	0.058	0.011
CuO	0.048	0.009	0.048	0.009
ZnO	0.020	0.004	0.220	0.004

4. Efficacy Studies for Water

Nanoparticles have been applied in several environmental contamination remediation processes. The spectrum of application is very broad, depending upon the nanoparticles, their functionalization, and the form of catalysis employed. As an example, mesoporous silica (mSiO₂) in conjunction with bismuth vanadate (BiVO₄) nanoparticles were used as photocatalysts for the degradation of methylene blue (MB) and brilliant green (BG) dyes as a function of mSiO₂ content [70]. Additionally, pure and modified mesoporous TiO₂ nanoparticles with different loadings of NiO were applied for photodegradation and hydrogen evolution [71].

In the present investigation, most of the materials are procured from commercial vendors, or synthesized using processes that are not environmentally friendly and/or do not follow green synthesis principles [12,13]. In our ongoing investigation, we have used agricultural waste to produce nanoparticles, using green processes to remove contaminants from the aquatic environment. This process is not only environmentally friendly but also environmentally responsible. Although there is a cost associated with agricultural waste removal, for these experiments, the waste was made freely available at no cost to the authors. These nanoparticles produced using the procedure as described here, serve as adsorbents to capture contaminants from the aquatic environment. It is worth noting that with the exception of our research group, only limited studies exist in the literature that focus on the synthesis of nanoparticles that are synthesized from agricultural wastes, using green chemistry principles, and are used for environmental contamination remediation. It is, therefore, critical that efficacy studies are conducted on SNPs produced using agricultural waste to study their effectiveness for the intended application. Several efficacy studies were carried out to mitigate long-chain hydrocarbons, including petroleum, and heavy metals in aquatic environments. This is an ongoing investigation and as the scope of applications expands further, this present set of investigations serves as the underlying basis for further investigations.

4.1. Petrol Remediation

It was observed that with a sorbent dose of 0.5 g at room temperature (25 °C) and at a pH value of 7, the petrol uptake efficiencies of nano-silica and nano-zeolite were measured at 95% and 85%, respectively [20]. The sorption rate for this investigation was calculated using the kinetic and isotherm models. The results showed that sorption is highly successful, and the percentage of pollutants eliminated is proportional to the amount of sorbent used. Second-order adsorption kinetics provided a more precise explanation of gasoline sorption; moreover, the Langmuir isotherms provided the most accurate description of sorption. The kinetic results also revealed that nano-silica and nano-zeolite (NZ) absorbed more gasoline; nevertheless, both sorbents reached saturation after 40 min of contact time. The study represents an important aspect since it represents the removal of aquatic pollutants

using nano-sorbents fabricated using agricultural waste, hence, enhancing environmental sustainability. These nanoparticles have a high affinity for gasoline impurities and might be used to remove oily/greasy contaminants in almost all types of aquatic settings, which could have been caused by accidental oil spills, sea harbor contamination, and other similar occurrences. Thus, by utilizing nano-silica and nano-zeolite for the removal of gasoline from polluted water, this study proposes a novel method with a better durability effect for the remediation of pollution originating from spills of gasoline and other petroleum products.

Application of Magnetic Nano-Silica on Diesel Oil

In another study [30], we studied the influence of contact time, and it was shown that the absorption of petrol pollutants began at 2 min at a rate of 20%, while increased sorption efficiency began at 5 min. The pollutant absorption rose to 65% after 8 min and 80% at 10 min. At 12 min, the greatest absorption rate of 85% was obtained, and the rate remained stable until the trial ended at approximately 22 min. This demonstrates that the sorption of petrol pollutants using magnetic nano-silica takes about 12 min to reach equilibrium. The sorption experiment progressed in time, indicating that sorption increased as time passed until the equilibrium time was attained. Low percentages of petroleum impurities were absorbed by nano-silica at low pH values of between 4 and 6, and due to the dependency of the pH value of the solution, the efficacy of petroleum mitigation was studied and documented. At pH 6, the absorption of pollutants began to increase, and by pH 7, the uptake had reached its peak. However, as the pH was raised further, the uptake efficiency began to decrease, with a substantial reduction in uptake observed between pH 8 and 10; hence the ideal pH for the adsorption of petroleum pollutants by MNSPs is ~pH 7, according to this study.

4.2. Heavy Metal Remediation—A Case Study of Nickel

Heavy metal pollution is a serious environmental issue around the world. Globally, more than five million soil sites are heavily contaminated with HMs [72]. Soil serves as a major sink of HMs released into the environment. Unlike organic contaminants, HMs are biologically or chemically non-degradable. However, their chemical forms and bioavailability are changeable [73]. Therefore, they can accumulate and remain persistent for long periods of time, posing serious environmental threats [73,74]. Hence, we conducted investigations to study the effect of contact time in order to estimate the equilibrium time for nickel adsorption onto barley nano-silica (NS-B) and wheat nano-silica (NS-W). The adsorption was quick at first, but it gradually slowed over time until it reached equilibrium after 65 min. This might be owing to the fact that there are more vacant sites available at the beginning of the process than at the end. Nickel (II) ion adsorption was measured at nickel concentrations of 10, 25, 50, 100, and 200 mg/L. With a remarkable 95% absorption efficiency, adsorption capabilities rise with nickel content. Furthermore, when the nickel starting concentration increased the effectiveness of NS-B removal dropped. A comparable drop in NS-W was also found. At 10 mg/L, the maximum adsorption efficiency was 95% for NS-B and 82% for NS-W. At pH 8.0, the largest proportion of adsorption was observed, with adsorption decreasing steadily as alkalinity increased (~pH 10). Due to the greater number of positively charged sites in the NS, contaminant adsorption was reduced at a lower pH. The number of negatively charged sites grows as the pH rises, making nickel adsorption easier. At a nickel concentration of 10 mg/L, the adsorbent dose was investigated by altering the adsorbent amount from 1 to 50 mg. These results demonstrate that the maximal adsorption efficiency began at 10 mg, after which the adsorption capacity of both barley and wheat NS remained relatively constant. The adsorptive potential of accessible NS-B was not completely explored at higher adsorbent doses compared to lower adsorbent dosages, resulting in a small decrease in Ni adsorption on NS-B with 35 mg addition. Table 3 shows results obtained from the application of NSPs prepared using different sources. Similar investigations are in progress for other metals and results will be presented in the future.

Table 3. Results from the applications of nano-silica particles from different sources.

Nanoparticle	Removal Efficiency	Equilibrium Time	Kinetic Model	Isotherm	Contaminant	Reference
Barley-grass-synthesized nano-amorphous silica	90%	65 min	1st Order	Freundlich	Nickel	[19]
Wheatgrass-synthesized nano-amorphous silica	85%	65 min	1st Order	Freundlich	Nickel	[19]
Barley-husk-grass-synthesized nano-amorphous silica (hydrophobic)	90%	60 min	2nd Order	Langmuir	Diesel oil	[30]
Barley-grass-synthesized nano-amorphous silica (magnetic)	85%	12 min	2nd Order	Langmuir	Petrol	[20]
Rice-husk-synthesized nano-amorphous silica	90%	25 min	-	-	Nickel catalyst	[18]

4.3. Reusability of Synthesized Nano-Silica

In Table 4, we provided the relevant information for the reusability analysis of nanoparticles. It was critical to articulate how the produced nanoparticles may be used in a sustainable manner. Experiments on reusability were carried out to see how many times each nanoparticle might be reused. When compared to non-reusable sorbents, reusable sorbents offer a much higher economic return value. In our study, the nanoparticles NS and NZ were utilized five times in a row. Nanoparticles were desorbed in n-Hexane after each usage to thoroughly eliminate any petroleum and then rinsed with distilled water before being used again.

Table 4. Reusability results of nanoparticles from different sources.

Nano-Silica	First Use	Second Use	Third Use	Fourth Use
Barley-grass-synthesized nano-amorphous silica	90%	90%	90%	90%
Wheatgrass-synthesized nano-amorphous silica	85%	85%	85%	75%
Barley-husk-grass-synthesized nano-amorphous silica (hydrophobic)	90%	90%	90%	90%
Barley-grass-synthesized nano-amorphous silica (magnetic)	85%	85%	85%	85%
Rice-husk-synthesized nano-amorphous silica	90%	90%	90%	85%

The nanoparticles' effectiveness decreased after the fourth cycle, indicating that they may be safely reused four times. To be categorized as a sustainable material, a material must fulfill certain reusability standards. Reusable sorbents are more cost-effective and easier to use since they may be reused repeatedly [75–77]. The rate of efficiency of magnetic nano-silica after five uses indicated that the adsorbent remained consistently potent after four uses, but the percentage of sorption reduced after the fifth use.

Further investigations show that acetic acid is the best solvent for desorption in reusability testing. Desorption studies were carried out by dissolving the depleted NS in acetic acid and stirring the solution for 70 min at 35 °C in a water bath and this technique

was repeated after each use of fresh acetic acid. After four cycles, the reusability efficiency declined slightly for wheat- and rice-husk-synthesized nano-silica after the fourth use while remaining the same for nano-silica from other sources. The number of cycles reflects each use after desorption, and the percentage of sorption efficiency for NS-B and NS-W remained impressive from reuse cycles 1 to 8, with 95–91% and 82–77% sorption, respectively.

5. Challenges and Future Pathways

Several high-cost processes involving surfactants are generally used to make commercial silica nanoparticles. Furthermore, the use of acid washing at high temperatures and pressures increases the cost of production, while also contributing to concerns related to environmental pollution and global warming. Thus, a simple and economically effective waste utilization and waste reduction technique used to produce nano-silica particles that are both inexpensive and less energy intensive than commercially available nano-silica appears to be a viable solution. As a result, a new initiative of using agricultural waste as a precursor for nano-silica production was undertaken in the present investigation. While converting agricultural waste into a sophisticated technology for environmental applications may appear to be a compelling circular economy solution, there are considerable knowledge gaps. The ability to preserve the material's properties and quality consistency is a big concern. Chemical approaches for the production of silica nanoparticles remain attractive due to their simplicity of control and high-purity product. However, only a few researchers have examined the synthesis and growth mechanisms that lead to the production of various forms of silica nanoparticles. There are currently no broad rules that can be used to guide the design and synthesis of products that fulfill specific functional needs. As a result, better knowledge and control of the synthesis process are required to assure product repeatability. Agricultural waste collection in large quantities can also be challenging, as these wastes are not always immediately available and there are costs associated with storing, transporting, and sorting, as farmers and producers would normally dispose of them at the farm waste site. Using the procedure, outlined here, the nanoparticles can be produced at the laboratory scale, since most nanoparticles begin to cluster during the production chain because of mechanical coupling, charge transfer, or elevated interfacial charge. Finding a way to prevent nanomaterial agglomeration, especially during the functionalization, would also facilitate the transition from the lab to the market. The ease of the synthesis process, ecologically benign silica precursor, and cheap cost of raw material are all key characteristics of using biodegradable materials to generate sustainable and eco-friendly silica nanoparticles. The cost-benefit analysis of commercially producing nano-silica is beyond the scope of the current investigation, however, is planned as an independent investigation.

6. Conclusions

Agricultural waste, in general, is less harmful than industrial waste. However, agricultural waste is disposed of in many forms, including burning which is commonly used to reduce the size of the waste. Since it produces GHG, it is vital to investigate ways to use such waste in a sustainable manner. The production of very pure nano-silica powder from rice husk, barley husk, barley grass, and wheatgrass is highlighted in the review. Various techniques were used, all with the objective of achieving a sustainable synthesis process to produce nano-silica, as well as meeting the target of waste eradication. To evaluate the synthesized silica nanoparticles, multiple characterization methods were utilized to establish the chemical composition, size, and shape. The significance of the numerous studies was their use of agricultural waste products as precursor raw materials. Acid reflux and heat management techniques were used to create magnetic micro-silica particles from wheat husk byproducts. Reflux and heat-treatment techniques were used to make nano-silica and nano-zeolite from wheatgrass. For the synthesis of nano-silica from barley and wheatgrass, processes based on green chemistry sustainable techniques were utilized, while for the synthesis of nano-silica from rice husk, an acid-leaching approach was used. Using the

procedures outlined in this paper, it is feasible to successfully synthesize high-purity silica nanoparticles. The nanoparticles produced for this investigation were used for contaminant uptake, especially in aquatic environments. Diesel, petrol, and heavy metals, such as nickel, were studied as the pollutants, with a removal efficiency between 85 and 90%. Additionally, the research showed that the silica nanoparticles were reusable even after four cycles, and SNPs fabricated using wheatgrass showed a 10% reduction after the fourth use. The results showed that the nanoparticles being used as adsorbents were quite successful in removing a considerable percentage of pollutants. Since the nano-sorbents were synthesized from waste products of plants and agricultural materials, our research objectives were clearly achieved which were to study the sustainable impact of SNPs using green synthesis and for a greener environment. An assessment of the effectiveness of nanoparticles for reuse was an important component of the study and the results indicated an average cycle of four reuses was observed for all nanoparticles. Although an economic analysis of translating the synthesis process to commercial production is beyond the scope of the current investigation, it is vital, and the authors intend to conduct a value proposition and economic feasibility assessment in our ongoing studies.

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