GREEN CHEMISTRY LETTERS AND REVIEWS
2024, VOL. 17, NO. 1, 2422416
https://doi.org/10.1080/17518253.2024.2422416

Taylor & Francis
Taylor & Francis Group

REVIEW ARTICLE

OPEN ACCESS Check for updates

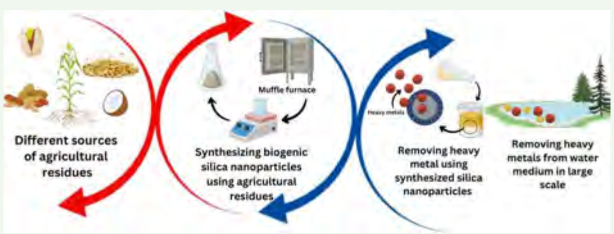
Synthesis of silica nanoparticles (SiNPs) from agro-wastes for removal of heavy metals from an aqueous medium – a mini review

Senthilvel Barani[a], Selvaraj Paul Sebastian[b], Periyasamy Dhevagi[a], Mohan Prasanthrajan[a] and Angappan Suganthi[c]

[a]Department of Environmental Sciences, Tamil Nadu Agricultural University, Coimbatore, India; [b]Department of Soil Science and Agricultural Chemistry, Agricultural College and Research Institute, Tamil Nadu Agricultural University, Kudumiyanmalai, India; [c]Department of Agricultural Entomology, Tamil Nadu Agricultural University, Coimbatore, India

ABSTRACT

Heavy metals are micropollutants, persist in the environment and accumulate in organisms, causing adverse effects to ecosystem. Synthetic inorganic minerals, polymers, activated carbon, ash, char, biomass powders, shells, etc. are used as adsorbents to remove the heavy metals in aqueous medium. Advancements in nanotechnology and green chemistry focus on novel materials for efficient removal of heavy metals. Among the different interesting nanomaterials, Silica nanoparticles (SiNPs) have recently emerged as an important nanomaterial used for environmental remediation due to their tractable pore size, distinct surface area, surface reactivity, outstanding biocompatibility, structural flexibility, stability, low toxicity, and adoptable surface modification. Due to the huge availability of biomass, SiNPs synthesis from crop residues and agro-industries waste by-products has been widely suggested. The SiNPs could be synthesized from agro-waste through calcination, sol-gel, ball milling, etc. Some of the SiNPs produced from certain agro-waste recorded a specific surface area of 5 to 653 m^2 g^{-1} with a particle size of sub-50 nm. These SiNPs remove a wide range of heavy metals, viz., Cr, Ni, Pb, Cd, As, Hg, Zn, etc., from aqueous solutions with varied concentrations. This review briefly discusses various agro-waste sources for SiNPs green synthesis and SiNPs heavy metal adsorption.



ARTICLE HISTORY
Received 25 March 2024
Accepted 23 October 2024

KEYWORDS
Silica nanoparticles; agricultural waste; synthesis; heavy metals; adsorption

1. Introduction

With the growing unease towards environmental pollution that deteriorates the earth's surface, heavy metals are considered the major source of contaminants in natural water systems (1). Heavy metals are released into the water through sewage water (2), diverse industrial effluent discharge, *i.e.* fertilizers, steel, dyes, batteries, mining, textiles, leather, alloying, electroplating, tannery, paper, food and cosmetics (3) and runoff (4). The most significant heavy metals are lead (Pb), zinc (Zn), mercury (Hg), nickel (Ni), cadmium (Cd), copper (Cu), chromium (Cr) and arsenic (As) (5). The metals are non-degradable and can enter the human system through the food chain and cause deleterious effects on human health due to their high toxicity, carcinogenicity and bio-recalcitrance (6). The maximum permissible limits prescribed by WHO and USEPA are given in Table 1. These heavy metals further concentrate at different trophic levels in the ecosystem and result in amplified harmful effects (7). In relation, Minamata Bay has shown us the evidenceof this pollution (8,9). Hence, the removal of heavy metals from the water is mandatory. Numerous treatment methods, *i.e.* absorption, adsorption, membrane, chemical, electric and

CONTACT Selvaraj Paul Sebastian paulsebastian.s@tnau.ac.in Department of Soil Science and Agricultural Chemistry, Agricultural College and Research Institute, Tamil Nadu Agricultural University, Kudumiyanmalai, Tamil Nadu, India

photocatalytic-based treatment, are adopted for the removal of heavy metals from water (5). Some of the popular heavy metal removal methods in aqueous medium are ultrafiltration, coagulation, flocculation, adsorption, absorption, membrane filtration, ion exchange, neutralization, solvent extraction, chemical precipitation, magnetic field implementation, electrochemical treatments and advanced oxidation processes (5,10,11). Among the different removal methods, adsorption is a widely adopted method since it is a cost-effective method, does not leave secondary waste and also shows promising efficiency (12,13). Absorbent ability can be increased by modifying its surface's physical and chemical properties towards heavy metal removal (14). Natural adsorbents, synthetic inorganic minerals, activated carbon, functionalized polymers and plant biomass-based adsorbents like powdered leaves, peel, bark, husk and shells have been used widely and extensively (15–19).

Table 1. Permissible limits for different heavy metals in wastewater treatment effluents according to the World Health Organization (20) and United States Environmental Protection Agency (USEPA) (21).

Heavy Metal	Permissible Limits (WHO) µg/L	Permissible Limits (USEPA) µg/L	Health Hazards
Arsenic	500	*	Carcinogenic, produce liver tumours, skin and gastrointestinal effects
Mercury	1	0.03	Corrosive to skin, eyes and muscle membrane, dermatitis, anorexia, kidney damage and severe muscle pain
Cadmium	3	10	Carcinogenic, cause lung fibrosis, dyspnea and weight loss
Lead	10	6	Suspected carcinogen, loss of appetite, anemia, muscle and joint pains, diminishing IQ, cause sterility, kidney problem and high blood pressure
Chromium	50	50	Suspected human carcinogen, producing lung tumours, allergic dermatitis
Nickel	20	200	Causes chronic bronchitis, reduced lung function, cancer of lungs and nasal sinus
Zinc	5000	*	Causes short-term illness called 'metal fume fever' and restlessness
Copper	3000	*	Long term exposure causes irritation of nose, mouth, eyes, headache, stomach-ache, dizziness, diarrhea

* Data not available.
(10).

Some sustainable adsorbents are activated carbon compounds like nanographene, hydrochar (22,23), nanobiochar (18), charcoal and other silica compounds like silica nanoparticles, magnetic silica particles, silica nanocomposites and silica cellulose particles (24). Although a good absorbent must possess the following abilities and capabilities, including well-engineered pore size and conformation, active adsorption sites, target-specific metal binding sites, durable and suitable for recycling (25). Currently, multiple types of nanoparticles, such as chitosan, carbonaceous, metallic, bimetallic, metal oxide, polymer-based, ferrite, magnetic and zeolite (26), are used as adsorbents and they significantly remove the heavy metals from aqueous mediums due to their high specific surface area, numerous reactive sites and low flocculent generation (27). Recently, using mesoporous silica nanoparticles (MSNPs), is a popular and versatile approach for heavy metal removal (28). Silica-based NPs are metal oxide nanoparticles having distinct features, which are shape-shifters at different oxidation states, tractable pore size, distinct surface area, outstanding biocompatibility and adaptable surface modification (14) for adsorption of heavy metals and they are an eco-friendly and non-toxic adsorbent (24,29,30). The adsorbents, such as mesoporous silica nanoparticles (MSNPs) can be simply recovered and reused (24). Silica nanoparticles (SiNPs) range from 1 to 1000 nm in particle size and contain large surface area, which acts as a site for heavy metal binding and is an excellent carrier material (31). Due to advancements in material science, green chemistry and sustainable development goals, researchers are getting involved in the green synthesis of nanomaterials from green materials for divergent applications (16). Agricultural crop residues and agro-industry waste materials have significant concentrations of silica. Synthesis of SiNPs from these materials is getting attention in recent days due to its desirable properties and its wide range of applications (25,32,33).

Approximately one billion metric tons of agricultural waste are produced worldwide each year; as an alternative approach, agricultural waste could be used as a source for silica production (34). The global market for sodium silicate was valued at around \$11.07 billion in 2022. It is estimated to reach around \$14.1 billion by 2030 (35) and it shows significant future market trends. Perhaps agricultural waste generation has been one of the main concern in disposal and management. So, there is a need to reduce this bulk-generated waste and repurpose this waste into green process-derived goods like silica nanoparticles (SiNPs). Agriculture generates a lot of trash, including rice husk, wheat straw, sugarcane bagasse and others (36). These residues are high in silica, particularly in the form of phytoliths and biogenic silica, which can be easily extracted and utilized (37). Synthesis of SiNPs from agro-waste offers an innovative strategy towards green synthesis . Amorphous, crystalline and also gel form of nano-size silica can be extracted from agro-wastes (38). Researchers mainly focus on the biogenic synthesis of SiNPs from different green wastes, which include sugarcane leaf (39), barley husk (40), rice husk (41), bamboo leaves (42) and groundnut shell (43). Diverse methods are available for SiNPs synthesis, such as acidic treatment (44), alkaline treatment (45), sol–gel method (44) and biological treatment (46), among which acidic, alkaline and sol–gel methods are widely used by researchers (47). The production of SiNPs from agro-waste products gives rise to the new green synthesis method and also opens avenue to minimize agriculture and agro-industry waste pollution (46) and achieve the sustainable development goal. Due to their large specific surface area, high porosity, chemical inertness and diverse set of surface functional groups (48,49), SiNPs have the ability to remove the heavy metals in an aqueous medium (48). Multiple researchers found that SiNPs and modified SiNPs (amino-functionalized SiNPs, silica nanoparticle spheres, non-functionalized SiNPs and amino-functionalized SiNPs gel) removed different heavy metals, *i.e.* Pb (II), Cd (II), Cu (II), Cr (VI) and Ni (II), from aqueous medium (24,30,50–52). Given this brief background, this mini-review illustrates the recent research on production methods of SiNPs from diverse agro-waste, characteristics of agro-waste-based SiNPs, its efficiency on removal of diverse heavy metals from aqueous solutions, heavy metal adsorption mechanisms and research gaps in this field.

2. General properties of silica nanoparticles (SiNPs)

Silica is one of the most abundant materials on earth and it is mostly found in sand, quartz and combined with other minerals (46). Silica is made up of four oxygen atoms with a central Si atom and forms a tetrahedral conformer, as illustrated in (Figure 1). Silica exists in both crystal and amorphous forms as SiO_2 (46). Silica is converted into nanosized particles by wide-ranging processes, which include physical ball milling and ultrasonication (53). SiNPs are typically between 10 and 500 nm in size, depending on the conditions in which that were kept constant during synthesis (38). It is possible to create SiNPs in varying sizes, forms and surface characteristics to suit a range of applications (54). The most prevalent forms of these silica nanoparticles with varying aspect ratios are nanorods and nanospheres. At the nanoscale, silica particles start to show unique properties not found in bulk silicon, such as antibacterial properties and a size-dependent photoluminescence (PL) (55). Because of its large surface area, silica nanoparticles (SiNPs) are perfect for several uses, such as supporting filler in the rubber sector (56). SiNPs are appealing because of their controlled pore size, huge surface area and adaptable structure (38). In 1990, the author created Folded Sheet Materials (FSM-16), a type of mesoporous silica with homogeneous pore sizes (57). The amalgamation of Santa Barbara Amorphous (SBA-15), a mesoporous material also shows great promise (58). The hexagonal structure of this highly structured material features thick pore walls and variable pore diameter (59). It appears to be a strong contender for separation procedures like adsorption as a result (48). In addition, functionalized silica nanoparticles are more effective at absorbing maximum capacity from an aqueous solution (60). Chemically grafting the surface has the effect of reducing the pore size of the changed materials, particularly when large or numerous functional groups are added (61). Mesoporous silica nanoparticles (MSNPs) synthesis is typically carried out by condensing a silica source in the presence of an appropriate template agent, removing the template and

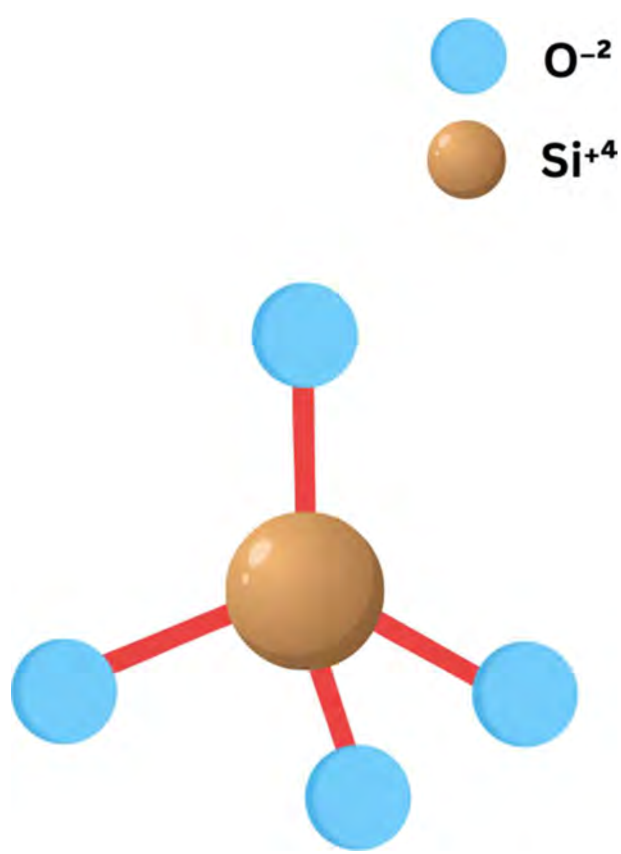


Figure 1. Silicate tetrahedral structure with four oxygen atoms.

then binding distinct functional groups onto the surface of the silica. This material is of great importance because of its enormous surface area (600–1000 m^2/g), limited distribution of pore sizes and substantial, regulated pore diameter (5–30 nm), which promote the fast adsorption kinetics of metal ions by facilitating their migration into the internal pore structure (62).

3. Assorted agro crop residue sources for SiNPs production

After harvesting, the residual crop material is called crop residues, which are straws, stubbles, weeds, leaves, seed pods, husks and processed waste such as sugarcane bagasse, sugarcane molasses and fly ashes that are used to produce SiNPs (46). Asian countries produce more crop residues, mainly Si-rich cereal crop residues and India generates approximately 500 metric tons of crop waste per year and about 1 billion tons of agricultural waste annually (36,63). Due to the high Si content in cereal crops, SiNPs production focused mainly on cereal crops (46,64–66). Crop wastes like wheat straw (67), barley husk (40), rice husk (41), sugarcane bagasse (68), corn cob husk (69), sorghum straw (70), bamboo leaves (42), groundnut shell (43) and coconut husk (45) can be used to synthesize SiNPs commercially (37). The major agricultural wastes used for the sustainable production of SiNPs are presented in Figure 2. The chemical composition of diverse agro-crop residues is tabulated in Table 2, which highlights the potential for SiNPs synthesis.

Figure 2. Different sources of silica nanoparticles (SiNPs) derived from agricultural waste.

4. Process for synthesizing of SiNPs from agro crop residues and its properties

Agriculture waste serves as a sustainable source for SiNPs production (25,32,33,38,44,51). Extensive research for producing SiNPs from agro-waste holds different processes such as microwave synthesis, heat extraction, reverse microemulsion refinement, strober's sol–gel method (71), acid treatment (72), alkali treatment (48), calcination (73) and mechanical treatment such as ball milling (74). Though strober's sol–gel gel is notably used as a prevalent top-down approach for the synthesis of SiNPs among researchers (75), SiNPs can be produced in two routes, *i.e.* thermal and chemical methods. Thermal methods utilize high temperatures to produce a crystalline form of silica, whereas chemical methods are classified as alkaline and acid treatments (76). The alkaline treatment produces a pure crystalline form and the acid treatment produces an amorphous form of silica (77). Alkaline reagents like NaOH react with biogenic silica present in agro-waste and produce homogenous monodispersed particles (78). On the other end, it results in poor hydrolysis due to the formation of crystalline form (79). This process can be better explained by the formation of bonds between sodium and silica (76). Further, this sodium silicate solution is hydrolysed using acid titration, due to which sol–gel is formed at neutral pH (80). Below neutral pH, silica gets precipitated as silicic acid and upon drying, crystalline structure is formed. Further other forms like hydrogel and silica sol can be synthesized using sodium silicate solution, by the addition of HCl and ammonia solution, respectively (81). Novel extractants of SiNPs from agro-waste mediated by organic acids, solvents and alkalis have the ability to degrade complexified structural compounds (82). Moreover, organic acids (citric acid, acetic acid and formic acid) are meant to be weak compared with inorganic acids (sulfuric, nitric, hydrochloric acids and phosphoric acid) involved in controlling the reaction kinetics (83–85). Surfactants largely influence the rate of condensation, nucleation, hydrolysis and additionally, they also help in controlling the size, surface area and pore dimension of SiNPs (86). Some of the size-stabilizing surfactants used for SiNPs from agro-wastes are cetyltrimethylammonium bromide (CTAB) (87) and polyethylene glycol (PEG) (88). The concentration of surfactant implies a distinguishable impact on pore size and surface area, where it is found that at higher concentrations particle size gets reduced to 2.62 nm with a mean surface area of 19.169 m^2 per g (89). The main reason behind the size reduction is due to the formation of micelles, where further it gets co-assembled with silica via hydrothermal or aging process (90). Moreover,

Table 2. Chemical composition of different agricultural residues.

S. No	Agricultural residues	Concentration (%) SiO$_2$	MgO	P$_2$O$_5$	K$_2$O	Fe$_2$O$_3$	CaO	Reference
1	Almond shell biomass ash	0.64	1.68	1.74	46.98	0.47	18.73	(124)
2	Banana peel ash	14.62	8.89	4.73	51.98	0.21	2.12	(125)
3	Banana peel ash	12.25	2.93	4.88	58.34	3.99	7.89	(126)
4	Coconut husk ash	11.65	–	0.08	18.32	0.40	29.71	(45)
5	Coconut shell ash	44.50	–	–	–	15.18	3.40	(127)
6	Coconut shell ash	37.99	1.84	0.32	0.82	15.48	4.98	(128)
7	Corn cobs	8.5	10.2	–	0.79	1.16	10.7	(129)
8	Date palm ash	52.35	0.1	–	15.52	13.36	11.72	(130)
9	Guinea corn husk ash	93.83	–	0.247	0.069	0.146	1.897	(70)
10	Kola nut shell ash	71.52	2.39	1.44	6.42	1.40	10.36	(131)
11	Orange peel ash	22.47	3.63	–	24.48	1.29	29.38	(132)
12	Palm ash	46.0	3.7	6.1	23.9	3.5	15.0	(133)
13	Palm kernel shell ash	55.69	4.85	2.39	9.71	3.32	11.21	(134)
14	Rice husk ash	80–90	0.5–2.0	–	0.2	0.5	1–2	(133)
15	Rice husk ash	87.9	1.26	–	5.58	0.33	3.40	(135)
16	Rice husk ash	94.1	0.26	0.56	1.67	0.79	0.98	(136)
17	Rice husk ash	84.14	0.44	–	1.34	1.15	0.97	(137)
18	Sugarcane bagasse ash	75.98	2.05	1.19	2.6	2.37	4.86	(138)
19	Sugarcane waste ash	88.68	0.288	–	–	1.688	0.117	(39)
20	Wheat straw	50–55	2.2–5	–	8–12	0.5–2	8–10	(139)
21	Cassava periderm	93.69	–	–	–	–	–	(44)
22	Maize stalk	90.63	–	–	–	–	–	(44)
23	Maize cob	59.10	–	–	–	–	–	(44)
24	Bamboo ash	37.69	–	–	–	–	–	(95)
25	Wheat straw	42.81	31.53	1.04	31.53	0.79	9.46	(67)
26	Wheat husk	41.27	29.59	1.12	29.59	0.79	7.59	

distinct shapes of SiNPs, for instance, spherical and rods. Further, these are classified as non-porous, mesoporous, hollow mesoporous and core–shell. When it comes to rod-shaped short and long rods, respectively (38).

Dosage and concentration of acid are helpful in the determination of SiNPs recovery rate from agro-waste. For example, SiNPs extracted from coconut shells evidenced a net yield of 0.237 mg higher than groundnut shell, banana peel, orange peel and walnut shell with usage of 20% sulfuric acid (91). Another important factor in stabilizing SiNPs has a critical role in maintaining the silica molecule interaction to form aggregates and agglomerates (92,93). In continuation, aggregates are difficult to break down, whereas agglomerates can be easily broken down due to the weak force of interaction and water bond (94). Hence, the common approach followed to reduce aggregates is the one-pot approach or template/grafting method as described by (95). One pot method refers to the fabrication of precursors such as native polymers to form nanocomposites to the core of already synthesized SiNPs (96). As a similar mechanism is described, zinc oxide-based SiNPs composites evidenced enhanced activity of capturing capacity with active sites of polyhydroxy functions (16). In the case of aggregates, it can be broken down using other conventional methods, such as ball milling on bamboo leaf-derived silica nanoparticles (SiNPs) using acetone, with a size of 1–5 nm followed by calcination and acid digestion with hydrochloric and sulfuric acid, which showed the highest pore volume of 0.918 cm^{3}per g at 2.5 N H_2SO_4 with a corresponding surface area of 544 m^2 per g, but increased surface area has been resulted at 1 N H_2SO_4 of 575 m^2 per g (95). As a contradiction, the above statement does not depend on the concentration of acids used to synthesis SiNPs might be due to aggregate formation (97).

The below chemical reaction explains the methods of extraction of SiNPs

Alkali based acid treatment

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$$

Silicon dioxide Sodium hydroxide Sodium Silicate Water

$$Na_2SiO_3 + H_2SO_4 \rightarrow SiO_2 + Na_2SO_4 + H_2O$$

Sodium Silicate Sulfuric acid Silicon dioxide Sodium Sulfate Water

Different methods are employed for synthesizing silica nanoparticles (SiNPs) from agricultural sources, as given in Table 3.

The surface characteristics are essential for SiNPs, as they mainly depend on surface area and pore size (98). High surface area initiates the SiNPs for diversified applications, including adsorption (60), catalysis (99) and drug delivery (100). So, as a result, waterborne contaminants can be efficiently removed, like heavy metals (101). An efficient SiNPs must possess the following properties for effective adsorption of metal contaminants: (i) chemical stability; (ii) surface charge; (iii) hydrophilicity; and (iv) thermal stability (60). Anuar et al. (45) reported that FESEM analysis on synthesized SiNPs showed that acid-

Table 3. Different agro-wastes and methods for synthesis of SiNPs.

S. No	Agricultural waste	Reagents and their concentration	Calcination temperature	Efficiency of Silica nanoparticles (SiNPs) produced	Methods	Reference
1	Bamboo leaves	1 N NaOH 3 M HCl	700 °C/ 3h	–	Sol-gel	(80)
2	Bamboo sticks and leaves	3 N NaOH 5 N H_2SO_4	700 °C/ 6h	45.73% and 79.93%, respectively	Sol-gel	(69)
3	Barley grass waste	10% HNO_3 2 M HCl	400, 500 °C 600, 700 °C	–	Sol-gel	(140)
4	Barley husk	2 M HCl 10% HNO_3	700 °C/ 5h	–	Sol-gel	(40)
5	Coconut husk	5 N H_2SO_4 2.5 N NaOH	–	91.76%	Sol-gel	(45)
6	Guinea corn husk	0.1 M HCl 2 M NaOH	650 °C/ 4h	93.83%	Sol-gel	(70)
7	Ragi husk	1 M HNO_3 3.0 M HNO_3	–	52.32%	Sol-gel	(141)
8	Rice husk	1 N NaOH 1 N HCl	500 °C/ 4h	–	Sol-gel	(47)
9	Rice husk	1 N NaOH 6 N HCl	–	91%	Sol-gel	(46)
10	Rice husk	0.5 M NaOH H_2SO_4	600 °C/ 4h	88.5%	Sol-gel	(41)
11	Rice husk	5% HCl 30% H_2SO_4 10% HCl	600 °C/ 4h	86.52%	Sol-gel	(31)
12	*Saccharum ravanae* Sugarcane Rice leaves	2.5 N NaOH 6 N HCl	450 °C/ 2h	64%	Sol-gel	(25)
13	Sugarcane bagasse	0.5% H_2SO_4 NaOH	–	–	Sol-gel	(68)
14	Sugarcane bagasse	15.5% H_2SO_4 13.3% NaOH	600 °C/ 6h	58.2%	Sol-gel	(102)
15	Sugarcane bagasse	1 M HNO_3 1 M NaOH	600 °C/ 6h	–	Sol-gel	(142)
16	Sugarcane bagasse	1 M HCl	950 °C/ 4h	30.21%	Sol-gel	(143)
17	Corn stalk		550 °C/ 4.5h	29.51%		
18	Rice husk		500 °C/ 4h	31.4%		
19	Sugarcane bagasse	Distilled water	650 °C/ 2h	9.52–21.25%	Hydro ball milling	(143)
20	Pine wood stem					
21	Walnut shell					
22	Rice husk					
23	Rice husk	0.5 M NaOH	600 °C/ 6h	–	Sol-gel	(144)
24	Bamboo leaves	1 N NaOH	–	–	Sol-gel	(111)

treated SiNPs were good, crystalline in their structure, whereas alkaline-treated SiNPs were smaller, irregular shapes and agglomerated together. This indicates that acid and alkali treatments produce different structures, such as crystalline and amorphous. TEM reveals that the structure of SiNPs synthesized using bagasse ash were clumps of nanosized less than 50 nm and EDX analysis exposed that silicon (Si) and oxygen (O) have a strong intensity where they form aggregate lumps (102). BET (Brunauer–Emmett–Teller) surface area analysis is an important method for determining the specific surface area of SiNPs. The surface properties of silica nanoparticles are shown in Table 4.

5. Adsorption efficacy studies of heavy metal on silica nanoparticles (SiNPs)

Heavy metals are considered one of the most predominant waterborne contaminants that cause serious harm to living organisms, both aquatic and terrestrial (103,104). SiNPs have been shown to lessen the phytotoxic effects of predominant heavy metals, including aluminium, arsenic, cadmium and chromium, by raising mineral content and antioxidant activities, while lowering the bioavailable concentration of metal ions (32). Hence, to eradicate those harmful pollutants, adsorbents such as silica nanoparticles (SiNPs) and functionalized silica nanoparticles (SiNPs) have also been successfully utilized to remove heavy metals from aqueous solutions (105). In terms of environmental application, major adsorption studies involved heavy metals such as Cr (IV) (106), Cd (II) (107), Pb (II) (108), Cu (II) (25), Ni (II) (109) and Fe (II) (110). The mechanism of heavy metal adsorption in silica nanoparticles (SiNPs) occurs in eight processes as shown in Figure 3.

Silica nanoparticles (SiNPs) act as an effective tool to remove heavy metal contaminants. Biogenic derived SiNPs are an emerging technique towards the removal

Table 4. Characteristics of SiNPs produced from different agro-waste.

S. No	Silica nanoparticles (SiNPs)	Specific surface area (m^2/g)	BET particle diameter (nm)	Density	Reference
1	Rice husk	245	50.6	–	(145)
2	Rice husk	164.0	–	–	(146)
3	Rice husk	164	25–30	2.22	(146)
4	Rice husk	653	1.98	0.646	(147)
5	Rice straw	7.2	100–120	–	(148)
	Rice hulls				
6	Ponni variety	538.10	1.167	1.98	(149)
7	Rice hulls (IR 20 variety)	423.20	1.132	1.53	
8	Rice hulls (CO 36 variety)	478.20	1.154	1.67	
9	Groundnut shell	56.7	35.6	–	(43)
10	Sugarcane waste	131	22	1.045	(39)
11	Barley grain	323	150	<0.10	(117)
12	Bamboo leaf	60.40	–	–	(80)
12	Palm kernel	438	2.2–6.3	–	(150)
13	Bagasse	20–30	30–40	–	(102)
14	Rice husk	300.20	8.5	0.659	(151)
15	Cornstalk	149	6.84	0.33	(143)
16	Rice husk	256	3.79	0.32	
17	Sugarcane bagasse	<5	25.0	0.01	
18	Teff straw	305	–	–	(152)
19	Wheat straw	32.04	154.216	0.013	(72)

process in a sustainable manner (111). For instance, lead (II) and chromium (VI) were successfully removed by using sol–gel-fabricated nano-silica oxide with the highest adsorption rates of 82.29% and 78.5%, respectively (24). Eventually, to enhance the adsorption rate, cationic binding sites are regulated where anionic metal ions get attached (112). Usually, SiNPs contain Si-OH bonds, which have a higher attraction to the harmful metal ions (113). Another study on chromium (VI) uptake by SiNPs expressed the highest adsorption capacity of 2.55 mg per g which exhibits different mechanisms such as electrostatic interaction, complexation,

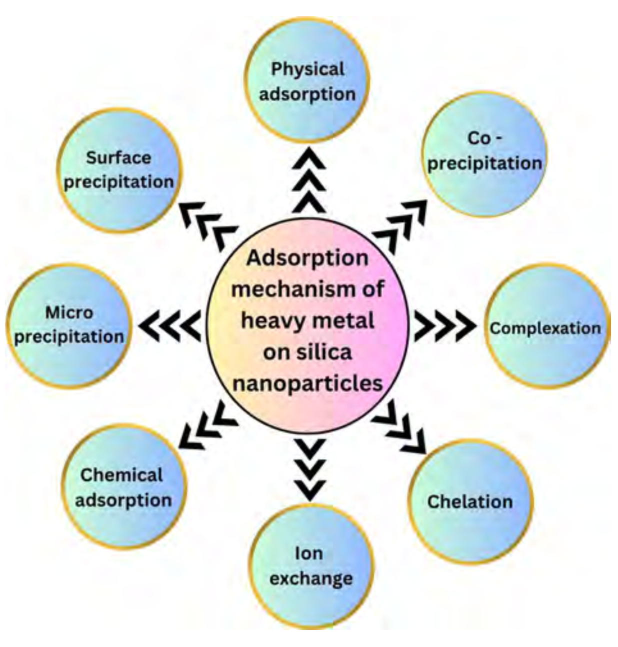


Figure 3. Heavy metal adsorption mechanism in silica nanoparticles (SiNPs).

functional group bonding [$Cr(OH)_3$] and reduction from Cr (VI) to Cr (III) as Cr-Si oxide formation (51).

To increase the rate of heavy metal adsorption, modification of SiNPs is necessary and widely adopted modifications of functional groups are siloxane, amino, carboxyl groups, polymers and Schiff's base (114). Iron immobilized with amino-modified SiNPs showed a surface area of 67.8 m^2g^{-1} and a pore size of 16.8 nm, which demonstrated good adsorption of Cd (II), Pb (II) and Ni (II) with a coefficient value of 0.99, which was well fitted under pseudo-second order (115). Similarly, amino group (3-aminopropyl) trimethoxysilane composite modified with dibenzoylmethane to the mesoporous silica nanoparticles (SiNPs), removed Cd (II), Hg (II) and Cu (II) with a removal rate of 35.37, 25.17 and 31.76 mg g^{-1}, respectively (48). The adsorption is mainly due to the formation of a stable five-member chelate ring with metal ions that surrounds the methylene CH_2 (C = N) functional group (48). The heavy metal removal by the functionalized SiNPs is shown in Table 5. Under acidic pH, the adsorbed heavy metals and SiNPs can be recovered and the desorption rate was recorded for Cd (II), Hg (II), Cu (II) as 99.12%, 99.07% and 98.37%, respectively, by using 0.5% HCl (v/v) (29). Although diverse functional groups are present, the target-specific heavy metals like Cr, Cd, Pb, Ni and Fe could be effectively removed by modified SiNPs, using $-NH_2$, -COOH and -SH groups, while also increasing their physical stability towards these metal ions (116). Other factors are pH, adsorbent dosage, the concentration of heavy metal and contact time influence of the SiNPs heavy metal adsorption rate. Nearly 96.9% of Cr (IV) adsorption was achieved at pH 4.0 and the lowest adsorption rate was observed at pH 2.0 and 7.0

Table 5. Functionalized silica nanoparticles (SiNPs) for different heavy metal removal in aqueous medium.

S. No	Type of SiNPs	Grafted material	Heavy metal utilized	Method	Removal efficiency	Reference
1	Diphenylcarbazide functionalized SiNPs	Diphenylcarbazide	Pb (II)	–	Showed high efficiency toward lead	(153)
2	PS-EDTA	Ethylenediaminetetraacetic acid (EDTA)	Pb (II)	Hydrothermal process	Pb (II) at pH 6 and 40 ppm with an adsorbent dosage of 0.5 g/L showed the highest removal rate of 99.98%.	(154)
3	$Fe_3O_4@SiO_2$	Polyvinyl alcohol (PVA)	Cu (II) Cd (II)	–	The highest adsorption rate was recorded at pH 7 with Cu (II) and Cd (II) of 1.57 and 0.99 mmol/g.	(155)
4	DTMSA adsorbent	1,2-ethane dithiol	Zn (II) Pb (II) Ni (II) Fe (II) Ni (II) Hg (II)	Co-condensation	Adsorbent showed selective adsorption of Hg ions with rate of 252 mg/g and 90% efficiency.	(156)
5	SiO_2	5-chloro-8-quinolinol	Al (III)	Refluxing	The highest adsorption rate of 95.06 mg/g was recorded for Al (III) ions.	(157)
6	A-SiO_2	3-(Aminopropyl)triethoxysilane	Cu (II)	Centrifugation	Unmodified SiO_2 reveals the highest rate of 121.95 mg/g and modified SiO_2 reveals 196.07 mg/g for Cu (II) ions.	(111)
7	MSNPs (Mesoporous Silica Nanoparticles) and LPMS (Large-Pore Mesoporous Silica)	3-(Aminopropyl)triethoxysilane 3-(Triethoxysilyl)propyl isocyanate	Fe (III) Ni (II) Cu (II)	Refluxing	Both adsorbents showed the highest removal rate.	(158)
8	MS-SBA-15	Melamine	Cr (VI)	–	Maximum adsorption capacity of 50 mg/g with efficiency of 84%.	(159)
9	Fe_3O_4 SBA-15	Imprinted Polymer using Methacrylic Acid	Pb (II) Cd (II)	Surface imprinting technique	Adsorption capacities of lead and cadmium shown that 10.28 mg/L and 10.38 mg/L	(160)
10	SiO2@poly (VI-co-AA)	1-vinyl-imidazole + acrylic acid	Ni (II)	Co-polymerization	Nickel (II) recorded an adsorption rate of 62.81 mg/g. With 30 mg/L of Ni (II) with a 99.40% significant removal rate.	(161)
11	Nano-SZO	Silica-based zinc oxide nanocomposites	Ni (II) Cu (II) Cd (II)	–	Maximum adsorption was recorded at pH 5.0 for Ni (II) with the rate of 0.4 g/L and Cd (II), Cu (II) at pH 6.0 with 0.4 g/L of total heavy metal concentration of 10 mg/L	(16)
12	MCM-48	Chitosan	U (VI) Sr (II)	Ultrasonication	Maximum retention capacities of 261.3 mg/g and 328.6 mg/g for U (VI) and Sr (II)	(162)
13	MCM-48–β-CD	β-cyclodextrin	As (V) Hg (II)	–	The highest adsorption rate of As (V) and Hg (II) with 265.6 and 207.9 mg/g, respectively.	(163)
14	SiO2/(3-aminopropyl)trimethoxysilane composite	Dibenzoylmethane	Hg (II) Cd (II) Cu (II)	Refluxing	The highest adsorption rate of Cd (II), Hg (II) and Cu (II) with 35.37, 25.17 and 31.76 mg/g, respectively.	(29)
15	Silica	Chitosan + PMMA (Polymethyl methacrylate)	Cr (VI)	–	Showed highest adsorption rate of 98% at pH 4	(164)
16	MCM-41	PVA (Polyvinyl alcohol)	Cd (II)	Ultrasonication	Resulted in increased efficiency towards Cd (II) removal Langmuir isotherm model adsorption rate of 46.73 mg/g	(165)
17	MSU-H	3-Aminopropyltrimethoxysilane (APTMS) 3-Glucidoxypropyltrimethoxysilane (GPTMS) 3-Methacryloxypropyltrimethoxysilane (MPTMS) Vinyltrimethoxysilane (VTMS) Phenyltrimethoxysilane (PTMS).	Hg (II) Pb (II) As (III) Cr (VI)	Direct co-condensation	The minimum and maximum adsorption efficiency of as follows 62–96%, 38–99%, 68–99%,	(166)

(*Continued*)

Table 5. Continued.

S. No	Type of SiNPs	Grafted material	Heavy metal utilized	Method	Removal efficiency	Reference
					79–93%, 67–98%	
18	SH-SBA-15 NH_2-SBA-15	3-Mercaptopropyl trimethoxysilane 3-Aminopropyl triethoxysilane	Pb (II) Cu (II)	Refluxing	SH-SBA-15 showed affinity towards Pb (II) and NH_2-SBA-15 showed towards Cu (II)	(167)
19	MCM-41 SDS-MCM-41	sodiumdodecylsulphate (SDS)	Cu (II) Zn (II)	–	SDS-MCM-41 showed a higher adsorption rate compared to MCM-41	(168)
20	SBA-15 1N-SBA-15 2N-SBA-15 3N-SBA-15	c-aminopropyl triethoxysilane (APTS), N-[3-(trimethoxysilyl)-propylethylene] diamine (TPED), trimethoxysilyl propyl diethylenetriamine (TPDT)	Hg (II) Pb (II) Cd (II) Cu (II) Zn (II)	Refluxing	1N-SBA-15 to 3N-SBA-15, showed adsorption capacities of Hg (II) rise from 382 mg/g to 726 mg/g	(61)

(51). Similar results were reported by Meky et al. (24) who stated that SiNPs absorbed maximum Cr (VI) at pH 1, whereas Ni (II) adsorption was maximum at pH 8 and it gradually reduced towards pH 10.0 (48) and the Pb (II) adsorption rate was maximum at pH 11 (24), which was mainly attributed to the zero-point charge on the siloxane group present on the SiNPs (24). Contact time is another important factor. Ni adsorption study revealed that among the different time intervals of 15, 30, 45, 60, 80, and 100 min, 60 min contact time recorded maximum removal efficiency of wheat and barley derived SiNPs (117). The pH directly affects the capturing capacity of silica nanoparticles (SiNPs) (118). For instance, pH demonstrated in Cr (VI) adsorption using horsetail, synthesized SiNPs with a range of 2.0–7.0 pH, where it showed the highest removal rate (96.9%) at pH 4 with a specific contact time of 60 min in an initial concentration of 50 mg L^{-1}. The main reason is due to the formation of metal ions in alkaline and acidic conditions. At alkali conditions, ions like $HCrO_4^-$, H_2Cr_4 and $Cr_2O_7^{2-}$ are removed whereas at acidic conditions, it is difficult to remove ions like CrO_4^{2-} (51,119). Also, the adsorption rate depends upon the charges of target metal ions. For example, Cu (II), Pb (II) and Cd (II) were adsorbed between pH 6 and 7, the isoelectric point of SiNPs. Below pH 2.0, cations are repelled due to positive charges present in both metal ions and adsorbents (120)). Adsorbent dosage also influences the rate of removal. Among the different adsorbent dosages (10–130 mg L^{-1}), 100 mg L^{-1} SiNPs recorded the highest removal (96.63%) of Cr (VI) metal ions in 100 mg L^{-1} concentration of Cr (VI). The reason behind this is that active adsorption sites are unfilled when it reaches 130 mg L^{-1} and at 10 mg L^{-1}, active sites are very few (51,111,121). Another similar research was carried out on Pb (II) and Cu (II) under 5–10 mg L^{-1} with the metal's concentration of 10 mg L^{-1}. In this, 5 mg adsorbent dosage recorded the highest adsorption of 99.5 mg $g^{-1}$and 97.52 mg g^{-1} for Pb (II) and Cu (II), respectively. Hence saturation of active sites is the main reason for this removal rate (25,122). Time also implies an important factor affecting the adsorption rate of heavy metal ions. Two SiNPs obtained from barley and wheat were used in the adsorption of Ni (II) with varied concentrations, *viz.*, 10, 25, 50, 100 and 200 mg L^{-1}. In this study, it was observed that 95% and 82% of Ni (II) were removed by barley-SiNPs and wheat-SiNPs at the contact time of 60 min (117). Less contact time and prolonged duration cause inferior adsorption, which may be insufficient time for adsorbent contact and re-escape from active sites of adsorbent surface, respectively. Temperature could also influence the heavy metal uptake mechanism.

Table 6. Various SiNPs derived from agro-waste used for heavy metal adsorption.

S. No	Type of agro-waste	Type of Si particle	Size	Type of heavy metal	Concentration	Removal efficiency	Bet surface area	Type of medium	Reference
1	Corn cob	Modified magnetic silica nanoparticles (SiNPs) coated iron	0.27 µm	Cr (VI)	10, 30, 50 and 100 mg/L from chromium stock solution of 1000 mg/L and absorbent dosage of 0.1 g	Maximum adsorption achieved about 97.4, 53.5, 39.5 and 24.6% with concentration of 11.39, 33.77, 56.51 and 114.71 mg/L	–	Synthetic water	(106)
2	Sugarcane bagasse	–	432 nm	Ni (II), Pb (II)	Studied batch adsorption experiments of adsorbent dosage, contact time, heavy metal ion concentration and pH on the adsorption efficiency at different concentrations.	At the maximum adsorption rate of Ni and Pb parameters reaches the highest level	–	Synthetic water	(108)
3	Crude corn cobs	–	–	Cd (II)	50 ml cadmium solution and with a concentration of 100 mg/L Adsorption kinetics experiment with 200 ml of cadmium solution concentration of 50 mg/L 0.5 g adsorbents were used for the study.	The highest adsorption recorded at 4.96 mg/g but functionalized SiNPs show even more 18.35 mg/g of cadmium ions	0.521 m^2/g	Synthetic water	(107)
4	Bamboo leaves	Crystalline structure	–	Cd (II)	The working concentration of Cd (II) is 100–500 mg/L	Maximum adsorption of Cd (II) is 133 mg/g	60.40 m^2/g	Synthetic water	(80)
5	Wheat grass Barley grass	NS-W NS-B	NS-W – 102nmNS-B – 70nm	Ni (II)	Initial Wheat grass SiNPs a. Poultry rearing water – 22.47 ± 0.92 mg/L b. Agricultural water – 13.38 ± 0.92 mg/L Barley grass SiNPs a. Poultry rearing water – 22.47 ± 0.92 mg/L b. Agricultural water – 13.38 ± 0.92 mg/L Final Wheat a. Poultry rearing water –4.563 ± 0.56 mg/L b. Agricultural water – 0.669 ± 0.91 mg/L Barley grass SiNPs a. Poultry rearing water – 4.151 ± 0.83 mg/L b. Agricultural water – 0.558 ± 0.48 mg/L	Wheat grass a. Poultry rearing water – 80% b. Agricultural water – 95% Barley grass a. Poultry rearing water – 82% b. Agricultural water – 96%	Barley grass SiNPs –127m^2/g Wheat grass SiNPs – 73.85 m^2/g	Real water – Poultry rearing water and Agricultural water	(117)
6	Rice husk	-	50 nm	Fe (II)	Concentration of Fe (II) range of 0.2, 0.4, 0.6, 0.8 and 1.0 ppm	Maximum adsorption rate of 9 mg of Fe (II)	78 m^2/g	Synthetic water	(28)
7	Rice husk	SiO2/CH/Fe nanocomposite	40–150 nm	Vanadium	100 mg/L concentration of vanadium solution with 0.05 g of adsorbent used	89.8%	271 m^2/g	Synthetic water	(169)
8	*Saccharum ravannae* (SRL), *Saccharum officinarum* (SOL) and *Oryza sativa* (OSL)	Crystalline	SRL SNPs – 3.56 nm SOL SNPs – 39.47 nm OSL SNPs – 29.13 nm	Lead (II) Copper (II)	Pb (II) and Cu (II) adsorption concentration for SRL SNPs – 140.06 mg/ g and 149.25 mg/g SOL SNPs – 338.55 mg/g and 179.45 mg/g OSL SNPs – 334.7 mg/g and 274.02 mg/g	More than 95%	SRL SNPs – 39.989 m^2/g SOL SNPs – 9.555 m^2/g OSL SNPs – 178.11 m^2/g	Synthetic water	(25)

(*Continued*)

Table 6. Continued.

S. No	Type of agro-waste	Type of Si particle	Size	Type of heavy metal	Concentration	Removal efficiency	Bet surface area	Type of medium	Reference
9	Horsetail plant (*Equisetum arvense*)	Crystalline	15.01 nm	Chromium (VI)	Chromium concentration – 50 mg/L GS NPs – 100 mg/L Maximum adsorption was reached at 2.55 mg/g	87.9%	14.57 m^2/g	Synthetic water	(51)
10	Lemon peel	SiNPs	–	Cu (II), Fe (II)	20–500 mg/L concentration of copper and iron Absorbent concentration of 50 mg/L	Maximum adsorption of Cu (II) and Fe (III) is 68.36%, 65%, respectively	–	Synthetic water	(110)
11	Rice husk	Amorphous	< 100 nm	Cr (VI), Pb (II), Cd (II) Ni (II)	–	Chromium (VI) showed highest adsorption of 42.55 mg/g Cr (VI) > Pb (II) > Cd (II) >Ni (II)	–	Synthetic water	(109)

The ideal temperature is about 35–40 °C for metal removal by biogenic SiNPs. This mainly falls on hydrogen bonding and van der Waals force among metal and adsorbent interaction (117,123). The SiNPs derived from diverse agro-waste for the removal of various heavy metals are presented in Table 6.

6. Conclusion

Producing silicon nanoparticles (SiNPs) from agricultural waste shows potential for eliminating heavy metals from water. Converting agricultural wastes into silicon nanoparticles results in two advantages: repurposing waste materials and creating a potent and eco-friendly adsorbent for removing heavy metals. SiNPs possess distinctive characteristics, such as their elevated surface area and reactivity, which render them well-suited for adsorption purposes. The utilization of agricultural wastes as a starting material for silicon nanoparticle production by concept of sustainable development and waste valorization. The production of silicon nanoparticles from agricultural waste to remove heavy metals shows great promise in tackling environmental pollution issues. SiNPs have been developed as efficient adsorbents for removing heavy metals from contaminated water due to their simplicity in synthesis, financial viability and ease of surface changes. They have shown high levels of selectivity and absorption capability, but there is still a need for improvement in heavy metal adsorption in aqueous solutions.

Further research is needed to improve biocompatibility and environmental sustainability and scale up laboratory operations. Currently, there is a lack of research on this topic and effective techniques for recovering nanosorbents in their active form are needed. Additionally, successful adsorption requires SiNPs with a significant surface area. The optimal synthesis technique, surface coating composition and geometric arrangement of SiNPs will help to produce the right size and surface area. In the future, SiNPs could be functionalized into magnetic particles, increasing their reusability and effectiveness in wastewater treatment. This review finding, could open the way for heavy metal contamination remedial measures, which pose a serious issue to mankind and also answers the question in future research wherein new technologies might be developed to trap and capture metal ions adsorbed silica nanoparticles safely from water medium. It greatly helps to reduce the burden of water pollution in polluted sites, especially in economically underdeveloped countries and costs could also be reduced for adopting these technologies as green-derived silica nanoparticles could be cost-effective.

Acknowledgements

The authors acknowledge the Department of Environmental Sciences at the Tamil Nadu Agricultural University, Coimbatore, India for funding and resources that facilitated this review paper.

Disclosure statement

No potential conflict of interest was reported by the author(s).

References

[1] Sarker, A.; Al Masud, M.A.; Deepo, D.M.; Das, K.; Nandi, R.; Ansary, M.W.R.; Islam, A.R.M.T.; Islam, T. Biological and Green Remediation of Heavy Metal Contaminated Water and Soils: A State-of-the-Art Review. *Chemosphere* **2023,** 138861. https://doi.org/10.1016/j.chemosphere.2023.138861.

[2] Balkrishna, A.; Mishra, S.; Singh, S.; Rajput, S.K.; Rana, M.; Arya, V. Hazardous Consequences and Management of Heavy Metals in Sewage Sludge: An Overview.

[3] Wadhawan, S.; Jain, A.; Nayyar, J.; Mehta, S.K. Role of Nanomaterials as Adsorbents in Heavy Metal Ion Removal from Waste Water: A Review. *J. Water Process Eng*. **2020,** *33*, 101038.https://doi.org/10.1016/j.jwpe.2019.101038.

[4] Pandey, S.; Kumari, N. Impact Assessment of Heavy Metal Pollution in Surface Water Bodies. *Metals Water* **2023,** *2023*, 129–154. https://doi.org/10.1016/B978-0-323-95919-3.00004-5.

[5] Qasem, N.A.; Mohammed, R.H.; Lawal, D.U. Removal of Heavy Metal Ions from Wastewater: A Comprehensive and Critical Review. *NPJ Clean Water* **2021,** *4* (1), 1–15. https://doi.org/10.1038/s41545-021-00127-0.

[6] Anjum, A.; Mazari, S.A.; Hashmi, Z.; Jatoi, A.S.; Abro, R.; Bhutto, A.W.; Mubarak, N.M.; Dehghani, M.H.; Karri, R.R.; Mahvi, A.H. A Review of Novel Green Adsorbents as a Sustainable Alternative for the Remediation of Chromium (VI) from Water Environments. *Heliyon* **2023,** *9* (5). https://doi.org/10.1016/j.heliyon.2023.e15575.

[7] Danovaro, R.; Cocozza di Montanara, A.; Corinaldesi, C.; Dell'Anno, A.; Illuminati, S.; Willis, T.J.; Gambi, C. Bioaccumulation and Biomagnification of Heavy Metals in Marine Micro-Predators. *Commun. Biol.* **2023,** *6* (1), 1206. https://doi.org/10.1038/s42003-023-05539-x.

[8] Aziz, K.H.H.; Mustafa, F.S.; Omer, K.M.; Hama, S.; Hamarawf, R.F.; Rahman, K.O. Heavy Metal Pollution in the Aquatic Environment: Efficient and Low-Cost Removal Approaches to Eliminate Their Toxicity: A Review. *RSC Adv.* **2023**, *13* (26), 17595–17610.

[9] Chernysh, Y.; Chubur, V.; Ablieieva, I.; Skvortsova, P.; Yakhnenko, O.; Skydanenko, M.; Plyatsuk, L.; Roubík, H. Soil Contamination by Heavy Metals and Radionuclides and Related Bioremediation Techniques: A Review. *Soil Syst.* **2024,** *8* (2), 36. https://doi.org/10.3390/soilsystems8020036.

[10] Vidu, R.; Matei, E.; Predescu, A.M.; Alhalaili, B.; Pantilimon, C.; Tarcea, C.; Predescu, C. Removal of Heavy Metals from Wastewaters: A Challenge from Current Treatment Methods to Nanotechnology Applications. *Toxics* **2020,** *8* (4), 101. https://doi.org/10.3390/toxics8040101.

[11] Yadav, S.; Yadav, A.; Bagotia, N.; Sharma, A.K.; Kumar, S. Adsorptive Potential of Modified Plant-Based Adsorbents for Sequestration of Dyes and Heavy Metals from Wastewater – A Review. *J. Water Process Eng*. **2021,** *42*, 102148. https://doi.org/10.1016/j.jwpe.2021.102148.

[12] Almomani, F.; Bhosale, R.; Khraisheh, M.; Almomani, T. Heavy Metal Ions Removal from Industrial Wastewater Using Magnetic Nanoparticles (MNP). *Appl. Surf. Sci.* **2020,** *506*, 144924. https://doi.org/10.1016/j.apsusc.2019.144924.

[13] Santhosh, C.; Velmurugan, V.; Jacob, G.; Jeong, S.K.; Grace, A.N.; Bhatnagar, A. Role of Nanomaterials in Water Treatment Applications: A Review. *Chem. Eng. J.* **2016,** *306*, 1116–1137.

[14] Da'na, E. Adsorption of Heavy Metals on Functionalized-Mesoporous Silica: A Review. *Microporous Mesoporous Mater.* **2017,** *247*, 145–157.

[15] Esfandiar, N.; Suri, R.; McKenzie, E.R. Competitive Sorption of Cd, Cr, Cu, Ni, Pb and Zn from Stormwater Runoff by Five Low-Cost Sorbents; Effects of co-Contaminants, Humic Acid, Salinity and pH. *J. Hazard. Mater.* **2022,** *423*, 126938. https://doi.org/10.1016/j.jhazmat.2021.126938.

[16] Garg, R.; Garg, R.; Eddy, N.O.; Almohana, A.I.; Almojil, S.F.; Khan, M.A.; Hong, S.H. Biosynthesized Silica-Based Zinc Oxide Nanocomposites for the Sequestration of Heavy Metal Ions from Aqueous Solutions. *J. King Saud University-Sci.* **2022,** *34* (4), 101996. https://doi.org/10.1016/j.jksus.2022.101996.

[17] Huo, M.-X.; Jin, Y.-L.; Sun, Z.-F.; Ren, F.; Pei, L.; Ren, P.-G. Facile Synthesis of Chitosan-Based Acid-Resistant Composite Films for Efficient Selective Adsorption Properties Towards Anionic Dyes. *Carbohydr. Polym.* **2021,** *254*, 117473. https://doi.org/10.1016/j.carbpol.2020.117473.

[18] Parameswari, E.; Kalaiarasi, R.; Davamani, V.; Kalaiselvi, P.; Paulsebastian, S.; Ilakiya, T. Potentials of Surface Modified Biochar for Removal of Cr from Tannery Effluent and its Regeneration to Ensure Circular Economy. *Biorem. J.* **2024,** *28* (2), 172–190.

[19] Premalatha, R.; Parameswari, E.; Davamani, V.; Malarvizhi, P.; Avudainayagam, S. Biosorption of Chromium (III) from Aqueous Solution by Water Hyacinth Biomass. *Madras Agricul. J.***2019,** *106*, 12–21.

[20] World Health Organization, WHO. 2017, Drinking water quality guidelines. Retrieved 21 February 2024 from https://www.who.int/teams/environment-climate-change-and-health/water-sanitation-and-health/water-safety-and-quality/drinking-water-quality-guidelines.

[21] United States Environmental Protection Agency, USEPA. 2018, National primary drinking water regulations, Retrieved 22 February 2024 from https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations.

[22] Oumabady, S.; Selvaraj, P.S.; Kamaludeen, S.P.; Ettiyagounder, P.; Suganya, K. Application of Sludge-Derived KOH-Activated Hydrochar in the Adsorptive Removal of Orthophosphate. *RSC Adv.* **2021**, *11* (12), 6535–6543. 10.1039/d0ra10943f.

[23] Oumabady, S.; Selvaraj, P.S.; Periasamy, K.; Veeraswamy, D.; Ramesh, P.T.; Palanisami, T.; Ramasamy, S.P. Kinetic and Isotherm Insights of Diclofenac Removal by Sludge Derived Hydrochar. *Sci. Rep.* **2022,** *12* (1), 2184. https://doi.org/10.1038/s41598-022-05943-z.

[24] Meky, N.; Salama, E.; Soliman, M.F.; Naeem, S.G.; Ossman, M.; Elsayed, M. Synthesis of Nano-Silica Oxide for Heavy Metal Decontamination from Aqueous Solutions. *Water Air Soil Pollut.* **2024,** *235* (2), 154. https://doi.org/10.1007/s11270-024-06944-6.

[25] Sachan, D.; Ramesh, A.; Das, G. Green Synthesis of Silica Nanoparticles from Leaf Biomass and its Application to Remove Heavy Metals from Synthetic Wastewater: A Comparative Analysis. *Environ. Nanotechnol., Monitor. Manage.* **2021,** *16*, 100467. https://doi.org/10.1016/j.enmm.2021.100467.

[26] Karami, D.; Mahinpey, N. The Synthesis of Novel Zeolite Y Nanoparticles Using Mesoporous Silica with a Temperature Controlling Method. *Can. J. Chem. Eng.* **2014,** *92* (4), 671–675.

[27] Verma, R.; Asthana, A.; Singh, A.K.; Prasad, S. An Arginine Functionalized Magnetic Nano-Sorbent for Simultaneous Removal of Three Metal Ions from Water Samples. *RSC Adv.* **2017,** *7* (81), 51079–51089.

[28] Nguyen, T.T.; Ma, H.T.; Avti, P.; Bashir, M.J.; Ng, C.A.; Wong, L.Y.; Jun, H.K.; Ngo, Q.M.; Tran, N.Q. Adsorptive Removal of Iron Using SiO2 Nanoparticles Extracted from Rice Husk Ash. *J. Anal. Methods. Chem.* **2019,** *2019*.

[29] Khalifa, M.E.; Abdelrahman, E.A.; Hassanien, M.M.; Ibrahim, W.A. Application of Mesoporous Silica Nanoparticles Modified with Dibenzoylmethane as a Novel Composite for Efficient Removal of Cd (II), Hg (II), and Cu (II) Ions from Aqueous Media. *J. Inorg. Organomet. Polym. Mater.* **2020,** *30*, 2182–2196.

[30] Li, C.; Zhou, K.; Qin, W.; Tian, C.; Qi, M.; Yan, X.; Han, W. A Review on Heavy Metals Contamination in Soil: Effects, Sources, and Remediation Techniques. *Soil Sediment Contamination: An Int. J.* **2019,** *28* (4), 380–394.

[31] Shrestha, D.; Nayaju, T.; Kandel, M.R.; Pradhananga, R.R.; Park, C.H.; Kim, C.S. Rice Husk-Derived Mesoporous Biogenic Silica Nanoparticles for Gravity Chromatography. *Heliyon* **2023,** *9* (4). https://doi.org/10.1016/j.heliyon.2023.e15142.

[32] Mahawar, L.; Ramasamy, K.P.; Suhel, M.; Prasad, S.M.; Živčák, M.; Brestic, M.; Rastogi, A.; Skalicky, M. Silicon Nanoparticles: Comprehensive Review on Biogenic Synthesis and Applications in Agriculture. *Environ. Res.* **2023,** *116292*. https://doi.org/10.1016/j.envres.2023.116292.

[33] Yan, G.; Huang, Q.; Zhao, S.; Xu, Y.; He, Y.; Nikolic, M.; Nikolic, N.; Liang, Y.; Zhu, Z. Silicon Nanoparticles in Sustainable Agriculture: Synthesis, Absorption, and Plant Stress Alleviation. *Front. Plant Sci.* **2024,** *15*, 1393458. https://doi.org/10.3389/fpls.2024.1393458.

[34] Peng, X.; Jiang, Y.; Chen, Z.; Osman, A.I.; Farghali, M.; Rooney, D.W.; Yap, P.-S. Recycling Municipal, Agricultural and Industrial Waste Into Energy, Fertilizers, Food and Construction Materials, and Economic Feasibility: A Review. *Environ. Chem. Lett.* **2023,** *21* (2), 765–801.

[35] Department, S. R. (2023). Global Market Value of Sodium Silicate 2015–2030. Statista Research Department. Retrieved 29 February 2024 from https://www.statista.com/statistics/1244462/global-market-value-sodium-silicate/

[36] Meena, H.; Jat, S.; Meena, M.; Singh, S. Crop Residue Generation, Recycling and Its Management for Agricultural Sustainability, 2020.

[37] Karande, S.D.; Jadhav, S.A.; Garud, H.B.; Kalantre, V.A.; Burungale, S.H.; Patil, P.S. Green and Sustainable Synthesis of Silica Nanoparticles. *Nanotechnol. Environ. Eng.* **2021,** *6* (2), 29.

[38] Yadav, M.; Dwibedi, V.; Sharma, S.; George, N. Biogenic Silica Nanoparticles from Agro-Waste: Properties, Mechanism of Extraction and Applications in Environmental Sustainability. *J. Environ. Chem. Eng.* **2022,** 108550. https://doi.org/10.1016/j.jece.2022.108550.

[39] Rovani, S.; Santos, J.J.; Corio, P.; Fungaro, D.A. Highly Pure Silica Nanoparticles with High Adsorption Capacity Obtained from Sugarcane Waste Ash. *ACS Omega* **2018,** *3* (3), 2618–2627.

[40] Akhayere, E.; Vaseashta, A.; Kavaz, D. Novel Magnetic Nano Silica Synthesis Using Barley Husk Waste for Removing Petroleum from Polluted Water for Environmental Sustainability. *Sustainability* **2020,** *12* (24), 10646. https://doi.org/10.3390/su122410646.

[41] Kumari, M.; Singh, K.; Dhull, P.; Lohchab, R.K.; Haritash, A. Sustainable Green Approach of Silica Nanoparticle Synthesis Using an Agro-Waste Rice Husk. *Nat. Environ. Pollut. Technol.* **2023,** *22*(1), 477–487.

[42] Dirna, F.C.; Rahayu, I.; Maddu, A.; Darmawan, W.; Nandika, D.; Prihatini, E. Nanosilica Synthesis from Betung Bamboo Sticks and Leaves by Ultrasonication. *Nanotechnol., Sci. Appl.* **2020,** *13*, 131–136.

[43] Yaro, S.; Olajide, O.; Asuke, F.; Popoola, A. Synthesis of Groundnut Shell Nanoparticles: Characterization and Particle Size Determination. *Int. J. Adv. Manufact. Technol.* **2017,** *91*, 1111–1116.

[44] Adebisi, J.; Agunsoye, J.; Ahmed, I.; Bello, S.; Haris, M.; Ramakokovhu, M.; Hassan, S. Production of Silicon Nanoparticles from Selected Agricultural Wastes. *Mater. Today: Proc.* **2021,** *38*, 669–674.

[45] Anuar, M.F.; Fen, Y.W.; Zaid, M.H.M.; Matori, K.A.; Khaidir, R.E.M. Synthesis and Structural Properties of Coconut Husk as Potential Silica Source. *Results Phys.* **2018,** *11*, 1–4.

[46] Sarkar, J.; Mridha, D.; Sarkar, J.; Orasugh, J.T.; Gangopadhyay, B.; Chattopadhyay, D.; Roychowdhury, T.; Acharya, K. Synthesis of Nanosilica from Agricultural Wastes and its Multifaceted Applications: A Review. *Biocatal. Agricul. Biotechnol.* **2021,** *37*, 102175. https://doi.org/10.1016/j.bcab.2021.102175.

[47] Singh, S.P.; Endley, N. Fabrication of Nano-Silica from Agricultural Residue and Their Application. In *Nanomaterials for Agriculture and Forestry Applications*; Husen, A., Jawaid, M., Eds.; Elsevier: Netherlands, **2020**; pp. 107–134.

[48] Akhayere, E.; Kavaz, D.; Vaseashta, A. Efficacy Studies of Silica Nanoparticles Synthesized Using Agricultural Waste for Mitigating Waterborne Contaminants. *Appl. Sci.* **2022,** *12* (18), 9279.

[49] Diagboya, P.N.; Dikio, E.D. Silica-Based Mesoporous Materials; Emerging Designer Adsorbents for Aqueous

Pollutants Removal and Water Treatment. *Microporous Mesoporous Mater.* **2018,** *266*, 252–267.

[50] Kotsyuda, S.S.; Tomina, V.V.; Zub, Y.L.; Furtat, I.M.; Lebed, A.P.; Vaclavikova, M.; Melnyk, I.V. Bifunctional Silica Nanospheres with 3-Aminopropyl and Phenyl Groups. Synthesis Approach and Prospects of Their Applications. *Appl. Surf. Sci.* **2017,** *420*, 782–791.

[51] Mehmood, S.; Mahmood, M.; Núñez-Delgado, A.; Alatalo, J.M.; Elrys, A.S.; Rizwan, M.; Weng, J.; Li, W.; Ahmed, W. A Green Method for Removing Chromium (VI) from Aqueous Systems Using Novel Silicon Nanoparticles: Adsorption and Interaction Mechanisms. *Environ. Res.* **2022,** *213*, 113614.

[52] Najafi, M.; Yousefi, Y.; Rafati, A. Synthesis, Characterization and Adsorption Studies of Several Heavy Metal Ions on Amino-Functionalized Silica Nano Hollow Sphere and Silica Gel. *Sep. Purif. Technol.* **2012,** *85*, 193–205.

[53] Jafari, V.; Allahverdi, A.; Vafaei, M. Ultrasound-assisted Synthesis of Colloidal Nanosilica from Silica Fume: Effect of Sonication Time on the Properties of Product. *Adv. Powder Technol.* **2014,** *25* (5), 1571–1577.

[54] Choudhary, R.; Kaur, P.; Adholeya, A. Synthesis of Agro-Waste-Mediated Silica Nanoparticles: An Approach Towards Sustainable Agriculture. In Nanotechnology in Agriculture and Environmental Science; Deshmukh, S.K., Kochar, M., Kaur, P., Singh, P.P., Eds.; CRC Press: Boca Raton, **2022**; pp. 278–291.

[55] Rahman, I.; Vejayakumaran, P.; Sipaut, C.; Ismail, J.; Chee, C. Size-Dependent Physicochemical and Optical Properties of Silica Nanoparticles. *Mater. Chem. Phys.* **2009,** *114* (1), 328–332.

[56] Chen, F.; Hong, H.; Shi, S.; Goel, S.; Valdovinos, H.F.; Hernandez, R.; Theuer, C.P.; Barnhart, T.E.; Cai, W. Engineering of Hollow Mesoporous Silica Nanoparticles for Remarkably Enhanced Tumor Active Targeting Efficacy. *Sci. Rep.* **2014**, *4* (1), 5080. https://doi.org/10.1038/srep05080.

[57] Yanagisawa, T.; Shimizu, T.; Kuroda, K.; Kato, C. The Preparation of Alkyltrimethylammonium–Kanemite Complexes and Their Conversion to Microporous Materials. *Bull. Chem. Soc. Jpn.* **1990,** *63* (4), 988–992.

[58] Zhao, D.; Feng, J.; Huo, Q.; Melosh, N.; Fredrickson, G.H.; Chmelka, B.F.; Stucky, G.D. Triblock Copolymer Syntheses of Mesoporous Silica with Periodic 50 to 300 Angstrom Pores. *Science* **1998,** *279*(5350), 548–552.

[59] Weiping, C.; Lide, Z. Synthesis and Structural and Optical Properties of Mesoporous Silica Containing Silver Nanoparticles. *J. Phys.: Condens. Matter* **1997,** *9* (34), 7257. https://doi.org/10.1088/0953-8984/9/34/015.

[60] Li, H.; Chen, X.; Shen, D.; Wu, F.; Pleixats, R.; Pan, J. Functionalized Silica Nanoparticles: Classification, Synthetic Approaches and Recent Advances in Adsorption Applications. *Nanoscale.* **2021,** *13* (38), 15998–16016.

[61] Zhang, L.; Yu, C.; Zhao, W.; Hua, Z.; Chen, H.; Li, L.; Shi, J. Preparation of Multi-Amine-Grafted Mesoporous Silicas and Their Application to Heavy Metal Ions Adsorption. *J. Non-Cryst. Solids* **2007,** *353* (44–46), 4055–4061.

[62] Aguado, J.; Arsuaga, J.M.; Arencibia, A. Influence of Synthesis Conditions on Mercury Adsorption Capacity of Propylthiol Functionalized SBA-15 Obtained by Co-Condensation. *Microporous Mesoporous Mater.* **2008,** *109* (1–3), 513–524.

[63] Prasad, M.; Ranjan, R.; Ali, A.; Goyal, D.; Yadav, A.; Singh, T.B.; Shrivastav, P.; Dantu, P.K. Efficient Transformation of Agricultural Waste in India. *Contamin. Agricul.: Sources Impacts Manage.* **2020,** *(2020)*, 271–287.

[64] Arumugam, A.; Ponnusami, V. Synthesis of SBA-15 from Low Cost Silica Precursor Obtained from Sugarcane Leaf Ash and Its Application as a Support Matrix for Lipase in Biodiesel Production. *J. Sol-Gel Sci. Technol.* **2013,** *67*, 244–250.

[65] Okoronkwo, E.; Imoisili, P.; Olusunle, S. Extraction and Characterization of Amorphous Silica from Corn cob ash by sol-gel Method. *Chem. Mater. Res.* **2013,** *3* (4), 68–72.

[66] Rangaraj, S.; Venkatachalam, R. A Lucrative Chemical Processing of Bamboo Leaf Biomass to Synthesize Biocompatible Amorphous Silica Nanoparticles of Biomedical Importance. *Appl. Nanosci.* **2017,** *7*, 145–153.

[67] Kumar, P.; Nandi, B.K. Combustion Characteristics of High Ash Indian Coal, Wheat Straw, Wheat Husk and Their Blends. *Mater. Sci. Energy Technol.* **2021,** *4*, 274–281.

[68] Kauldhar, B.S.; Sooch, B.S.; Rai, S.K.; Kumar, V.; Yadav, S.K. Recovery of Nanosized Silica and Lignin from Sugarcane Bagasse Waste and Their Engineering in Fabrication of Composite Membrane for Water Purification. *Environ. Sci. Pollut. Res.* **2021,** *28*, 7491–7502.

[69] Goswami, P.; Mathur, J. Application of Agro-Waste-Mediated Silica Nanoparticles to Sustainable Agriculture. *Bioresour. Bioprocess.* **2022,** *9* (1), 1–12.

[70] Bello, M.; Abdus-Salam, N.; Adekola, F. Utilization of Guinea Corn (Sorghum Vulgare) Husk for Preparation of Bio-Based Silica and iTs Characterization Studies. *Int. J. Environ. Agricul. Biotechnol.* **2018,** *3* (2), 239116. https://doi.org/10.22161/ijeab/3.2.48.

[71] Saha, A.; Mishra, P.; Biswas, G.; Bhakta, S. Greening the Pathways: A Comprehensive Review of Sustainable Synthesis Strategies for Silica Nanoparticles and Their Diverse Applications. *RSC Adv.* **2024,** *14* (16), 11197–11216.

[72] Ramasamy, S.P.; Veeraswamy, D.; Ettiyagounder, P.; Arunachalam, L.; Devaraj, S.S.; Krishna, K.; Oumabady, S.; Sakrabani, R. New Insights Into Method Development and Characterization of Amorphous Silica from Wheat Straw. *Silicon* **2023,** *15* (12), 5049–5063.

[73] Nivaethaa, C.; Rajkishore, S.; Maheswari, M.; Sritharan, N.; Moorthy, P.; Prasanthrajan, M.; Subramanian, P.; Ravendran, M.; Rajamanickam, U.; Bhuyan, R.P. Synthesis and Characterization of Silica Nanoparticles Derived from Tea Factory Generated Wood Ash. *Int. J. Environ. Climate Change* **2024,** *14* (2), 340–352.

[74] F Hincapié Rojas, D.; Pineda Gómez, P.; Rosales Rivera, A. Production and Characterization of Silica Nanoparticles from Rice Husk. *Adv. Mater. Lett* **2019,** *10* (1), 67–73.

[75] Ren, G.; Su, H.; Wang, S. The Combined Method to Synthesis Silica Nanoparticle by Stöber Process. *J. Sol-Gel Sci. Technol.* **2020,** *96*, 108–120.

[76] Kasera, N.; Chatterjee, G.; Joshi, S.; Shah, P. Synthesis of Nano-Silica Material from Agricultural Wastes, 2023.

[77] Hossain, S.S.; Bae, C.-J.; Roy, P. Recent Progress of Wastes Derived Nano-Silica: Synthesis, Properties, and

Applications. *J. Cleaner Prod.* **2022,** *377*, 134418. https://doi.org/10.1016/j.jclepro.2022.134418.

[78] Bhakta, S.; Dixit, C.K.; Bist, I.; Jalil, K.A.; Suib, S.L.; Rusling, J.F. Sodium Hydroxide Catalyzed Monodispersed High Surface Area Silica Nanoparticles. *Mater. Res. Express* **2016**, *3* (7), 075025.

[79] Zaky, R.; Hessien, M.M.; El-Midany, A.; Khedr, M.; Abdel-Aal, E.; El-Barawy, K. Preparation of Silica Nanoparticles from Semi-Burned Rice Straw Ash. *Powder Technol.* **2008,** *185* (1), 31–35.

[80] Durairaj, K.; Senthilkumar, P.; Velmurugan, P.; Dhamodaran, K.; Kadirvelu, K.; Kumaran, S. Sol-Gel Mediated Synthesis of Silica Nanoparticle from Bambusa Vulgaris Leaves and Its Environmental Applications: Kinetics and Isotherms Studies. *J. Sol-Gel Sci. Technol.* **2019,** *90*, 653–664.

[81] Tessema, B.; Gonfa, G.; Hailegiorgis, S.M.; Prabhu, S.V. Synthesis and Characterization of Modified Silica Gel from Teff Straw Ash Using Sol-gel Method. *Next Mater.* **2024,** *3*, 100146. https://doi.org/10.1016/j.nxmate.2024.100146.

[82] September, L.A.; Kheswa, N.; Seroka, N.S.; Khotseng, L. Green Synthesis of Silica and Silicon from Agricultural Residue Sugarcane Bagasse Ash – A Mini Review. *RSC Adv.* **2023,** *13* (2), 1370–1380.

[83] Bari, A.H.; Jundale, R.B.; Kulkarni, A.A. Understanding the Role of Solvent Properties on Reaction Kinetics for Synthesis of Silica Nanoparticles. *Chem. Eng. J.* **2020,** *398*, 125427. https://doi.org/10.1016/j.cej.2020.125427.

[84] Chang, H.; Kim, J.; Rho, W.-Y.; Pham, X.-H.; Lee, J.H.; Lee, S.H.; Jeong, D.H.; Jun, B.-H. Silica Nanoparticles. *Nanotechnol. Bioappl.* **2021,** *1309*, 41–65.

[85] Idris, A.; Man, Z.; Maulud, A.S.; Bustam, M.A.; Mannan, H.A.; Ahmed, I. Investigation on Particle Properties and Extent of Functionalization of Silica Nanoparticles. *Appl. Surf. Sci.* **2020,** *506*, 144978.

[86] Candela-Noguera, V.; Alfonso, M.; Amorós, P.; Aznar, E.; Marcos, M.D.; Martínez-Máñez, R. In-Depth Study of Factors Affecting the Formation of MCM-41-Type Mesoporous Silica Nanoparticles. *Microporous Mesoporous Mater.* **2024**, *363*, 112840.

[87] Saman, N.; Othman, N.S.; Chew, L.-Y.; Setapar, S.H.M.; Mat, H. Cetyltrimethylammonium Bromide Functionalized Silica Nanoparticles (MSN) Synthesis Using a Combined Sol-Gel and Adsorption Steps with Enhanced Adsorption Performance of Oxytetracycline in Aqueous Solution. *J. Taiwan Instit. Chem. Eng.* **2020,** *112*, 67–77.

[88] Gramatges, A.P. Synthesis and Characterization of Fluorescent Silica Nanoparticles with Potential Application in Transport and Adsorption Studies in Porous Medium PUC-Rio, 2023.

[89] Rumiyanti, L.; Destiana, C.; Oktaviani, R.; Marjunus, R.; Suharyadi, E. Facile Pore Size Control and Low-Cost Synthesis of Mesoporous Silica Nanoparticles Based on Rice Husk. *Adv. Nat. Sci.: Nanosci. Nanotechnol.* **2023**, *14* (1), 015007. https://doi.org/10.1088/2043-6262/acc456.

[90] Pande, V.; Kothawade, S.; Kuskar, S.; Bole, S.; Chakole, D. Fabrication of Mesoporous Silica Nanoparticles and Its Applications in Drug Delivery. In *Nanofabrication Techniques-Principles, Processes and Applications*. IntechOpen, **2023**; Vol. 2023.

[91] Peerzada, J.G.; Chidambaram, R. A Statistical Approach for Biogenic Synthesis of Nano-Silica from Different Agro-Wastes. *Silicon* **2021,** *13*, 2089–2101.

[92] Kontou, E.; Christopoulos, A.; Koralli, P.; Mouzakis, D.E. The Effect of Silica Particle Size on the Mechanical Enhancement of Polymer Nanocomposites. *Nanomaterials* **2023,** *13* (6), 1095.

[93] Sharifzadeh, E.; Karami, M.; Ader, F. Formation of Nanoparticle Aggregates and Agglomerates in Polymer Nanocomposites and Their Distinct Impacts on the Mechanical Properties. *Polymer Eng. Sci.* **2023,** *63* (4), 1303–1313.

[94] Montini, D.; Cara, C.; D'Arienzo, M.; Di Credico, B.; Mostoni, S.; Nisticò, R.; Pala, L.; Scotti, R. Recent Advances on Porous Siliceous Materials Derived from Waste. *Materials (Basel)* **2023,** *16* (16), 5578.

[95] Dileep, P.; Narayanankutty, S.K. A Novel Method for Preparation of Nanosilica from Bamboo Leaves and Its Green Modification as a Multi-Functional Additive in Styrene Butadiene Rubber. *Mater. Today Commun.* **2020,** *24*, 100957. https://doi.org/10.1016/j.mtcomm.2020.100957.

[96] Bazzi, L.; Hesemann, P.; Laassiri, S.; El Hankari, S. Alternative Approaches for the Synthesis of Nano Silica Particles and Their Hybrid Composites: Synthesis, Properties, and Applications. *Int. J. Environ. Sci. Technol.* **2023,** *20* (10), 11575–11614.

[97] Liu, Y.; Tourbin, M.; Lachaize, S.; Guiraud, P. Silica Nanoparticles Separation from Water: Aggregation by Cetyltrimethylammonium Bromide (CTAB). *Chemosphere* **2013,** *92(6)*, 681–687.

[98] Li, G.; Liu, Q.; Niu, M.; Cao, L.; Nan, B.; Shi, C. Characteristic of Silica Nanoparticles on Mechanical Performance and Microstructure of Sulphoaluminate Cement/Ordinary Portland Cement Binary Blends. *Constr. Build. Mater.* **2020,** *242*, 118158.

[99] Singh, B.; Na, J.; Konarova, M.; Wakihara, T.; Yamauchi, Y.; Salomon, C.; Gawande, M.B. Functional Mesoporous Silica Nanomaterials for Catalysis and Environmental Applications. *Bull. Chem. Soc. Jpn.* **2020,** *93* (12), 1459–1496.

[100] Fang, L.; Zhou, H.; Cheng, L.; Wang, Y.; Liu, F.; Wang, S. The Application of Mesoporous Silica Nanoparticles as a Drug Delivery Vehicle in Oral Disease Treatment. *Front. Cell. Infect. Microbiol.* **2023,** *13*, 1124411.

[101] Dias, L.S.; Alves, A.K. Silica Nanoparticles: Morphology and Applications. *Technol. Appl. Nanomater.* **2022,** *1*, 89–106.

[102] Sholeh, M.; Rochmadi, R.; Sulistyo, H.; Budhijanto, B. Nanostructured Silica from Bagasse Ash: The Effect of Synthesis Temperature and pH on Its Properties. *J. Sol-Gel Sci. Technol.* **2021,** *97*, 126–137.

[103] Jeong, H.; Byeon, E.; Kim, D.-H.; Maszczyk, P.; Lee, J.-S. Heavy Metals and Metalloid in Aquatic Invertebrates: A Review of Single/Mixed Forms, Combination with Other Pollutants, and Environmental Factors. *Mar. Pollut. Bull.* **2023,** *191*, 114959. https://doi.org/10.1016/j.marpolbul.2023.114959.

[104] Rashid, A.; Schutte, B.J.; Ulery, A.; Deyholos, M.K.; Sanogo, S.; Lehnhoff, E.A.; Beck, L. Heavy Metal Contamination in Agricultural Soil: Environmental

Pollutants Affecting Crop Health. *Agronomy* **2023,** *13* (6), 1521. https://doi.org/10.3390/agronomy13061521.

[105] Mureseanu, M.; Reiss, A.; Stefanescu, I.; David, E.; Parvulescu, V.; Renard, G.; Hulea, V. Modified SBA-15 Mesoporous Silica for Heavy Metal Ions Remediation. *Chemosphere* **2008,** *73* (9), 1499–1504.

[106] Kumari, D.; Goswami, R.; Kumar, M.; Kataki, R.; Shim, J. Removal of Cr (VI) Ions from the Aqueous Solution Through Nanoscale Zero-Valent Iron (nZVI) Magnetite Corn Cob Silica (MCCS): A Bio-Waste Based Water Purification Perspective. *Groundwater Sustainable Develop.* **2018,** *7*, 470–476.

[107] Lin, H.; Xu, J.; Dong, Y.; Wang, L.; Xu, W.; Zhou, Y. Adsorption of Heavy Metal Cadmium (II) Ions Using Chemically Modified Corncob: Mechanism, Kinetics, and Thermodynamics. *Desalin. Water Treat.* **2016,** *57* (39), 18537–18550.

[108] Ifijen, I.H.; Itua, A.B.; Maliki, M.; Ize-Iyamu, C.O.; Omorogbe, S.O.; Aigbodion, A.I.; Ikhuoria, E.U. The Removal of Nickel and Lead Ions from Aqueous Solutions Using Green Synthesized Silica Microparticles. *Heliyon* **2020,** *6* (9). https://doi.org/10.1016/j.heliyon.2020.e04907.

[109] Mondal, M.I.H.; Chakraborty, S.C.; Rahman, M.S.; Marjuban, S.M.H.; Ahmed, F.; Zhou, J.L.; Ahmed, M.B.; Zargar, M. Adsorbents from Rice Husk and Shrimp Shell for Effective Removal of Heavy Metals and Reactive Dyes in Water. *Environ. Pollut.* **2024,** 123637. https://doi.org/10.1016/j.envpol.2024.123637.

[110] Eissa, D.; Hegab, R.H.; Abou-Shady, A.; Kotp, Y.H. Green Synthesis of ZnO, MgO and SiO2 Nanoparticles and Its Effect on Irrigation Water, Soil Properties, and Origanum Majorana Productivity. *Sci. Rep.* **2022,** *12* (1), 5780. https://doi.org/10.1038/s41598-022-09423-2.

[111] Sharma, P.; Kherb, J.; Prakash, J.; Kaushal, R. A Novel and Facile Green Synthesis of SiO2 Nanoparticles for Removal of Toxic Water Pollutants. *Appl. Nanosci.* **2023,** *13* (1), 735–747.

[112] Du, P.; Zhang, J.; Cai, Z.; Ge, F. High Adsorption of Cationic Dyes from Aqueous Solution Using Worm-Like Porous Nanosilica: Isotherm, Kinetics and Thermodynamics. *Mater. Today Commun.* **2023,** *35*, 105697. https://doi.org/10.1016/j.mtcomm.2023.105697.

[113] Siddeeg, S.M.; Tahoon, M.A.; Alsaiari, N.S.; Shabbir, M.; Rebah, F.B. Application of Functionalized Nanomaterials as Effective Adsorbents for the Removal of Heavy Metals from Wastewater: A Review. *Curr. Anal. Chem.* **2021,** *17* (1), 4–22.

[114] Munaweera, I.; Pathiraja, A.S.; Kottegoda, N. Surface Functionalized Mesoporous Silica Nanoparticles for Enhanced Removal of Heavy Metals: A Review. *Vidyodaya J. Sci.* **2023,** *1(s1)*, 24–44.

[115] Liu, Z.; Lei, M.; Zeng, W.; Li, Y.; Li, B.; Liu, D.; Liu, C. Synthesis of Magnetic Fe3O4@ SiO2-(-NH2/-COOH) Nanoparticles and Their Application for the Removal of Heavy Metals from Wastewater. *Ceram. Int.* **2023,** *49* (12), 20470–20479.

[116] Rafeeq, H.; Hussain, A.; Ambreen, A.; Waqas, M.; Bilal, M.; Iqbal, H.M. Functionalized Nanoparticles and Their Environmental Remediation Potential: A Review. *J. Nanostruct. Chem.* **2022,** *12* (6), 1007–1031.

[117] Akhayere, E.; Essien, E.A.; Kavaz, D. Effective and Reusable Nano-Silica Synthesized from Barley and Wheat Grass for the Removal of Nickel from Agricultural Wastewater. *Environ. Sci. Pollut. Res.* **2019,** *26* (25), 25802–25813.

[118] Ahmed, W.; Mehmood, S.; Núñez-Delgado, A.; Qaswar, M.; Ali, S.; Ying, H.; Liu, Z.; Mahmood, M.; Chen, D.-Y. Fabrication, Characterization and U (VI) Sorption Properties of a Novel Biochar Derived from *Tribulus terrestris* via Two Different Approaches. *Sci. Total Environ.* **2021,** *780*, 146617.

[119] Kekes, T.; Kolliopoulos, G.; Tzia, C. Hexavalent Chromium Adsorption Onto Crosslinked Chitosan and Chitosan/β-Cyclodextrin Beads: Novel Materials for Water Decontamination. *J. Environ. Chem. Eng.* **2021,** *9* (4), 105581.

[120] Zhu, W.; Wang, J.; Wu, D.; Li, X.; Luo, Y.; Han, C.; Ma, W; He, S.. Investigating the heavy metal adsorption of mesoporous silica materials prepared by microwave synthesis. *Nanoscale research letters*. **2017,** *12*, 1–9.

[121] Chabaane, L.; Tahiri, S.; Albizane, A.; El Krati, M.; Cervera, M.L.; De la Guardia, M. Immobilization of Vegetable Tannins on Tannery Chrome Shavings and Their use for the Removal of Hexavalent Chromium from Contaminated Water. *Chem. Eng. J.* **2011,** *174* (1), 310–317.

[122] Debnath, N.; Mitra, S.; Das, S.; Goswami, A. Synthesis of Surface Functionalized Silica Nanoparticles and Their Use as Entomotoxic Nanocides. *Powder Technol.* **2012,** *221*, 252–256.

[123] Okonkwo, E.C.; Essien, E.A.; Abid, M.; Kavaz, D.; Ratlamwala, T.A. Thermal Performance Analysis of a Parabolic Trough Collector Using Water-Based Green-Synthesized Nanofluids. *Sol. Energy* **2018,** *170*, 658–670.

[124] Soriano, L.; Font, A.; Tashima, M.M.; Monzó, J.; Borrachero, M.V.; Bonifácio, T.; Payá, J. Almond-Shell Biomass Ash (ABA): A Greener Alternative to the Use of Commercial Alkaline Reagents in Alkali-Activated Cement. *Constr. Build. Mater.* **2021,** *290*, 123251.

[125] Alaneme, G.U.; Olonade, K.A.; Esenogho, E. Discover Materials, 2023.

[126] Ali, N.M. The Effect of Plantain and Banana Peel Ash on the Properties of Concrete. *Open Access Repository* **2022,** *9* (04), 31–37.

[127] Bheel, N.; Chohan, I.M.; Ghoto, A.A.; Abbasi, S.A.; Tag-eldin, E.M.; Almujibah, H.R.; Ahmad, M.; Benjeddou, O.; Gonzalez-Lezcano, R.A. Synergistic Effect of Recycling Waste Coconut Shell ash, Metakaolin, and Calcined Clay as Supplementary Cementitious Material on Hardened Properties and Embodied Carbon of High Strength Concrete. *Case Stud. Construct. Mater.* **2024,** *20*, e02980.

[128] Abdelrahman, M.; Kugara, J. An Assessment of the Potential Use of Coconut Shell Ash (CSA) as a Cementitious Material. *Case Stud. Constr. Mater.* **2018,** *8*, 95–105.

[129] Pieła, A.; Żymańczyk-Duda, E.; Brzezińska-Rodak, M.; Duda, M.; Grzesiak, J.; Saeid, A.; Mironiuk, M.; Klimek-Ochab, M. Biogenic Synthesis of Silica Nanoparticles from Corn Cobs Husks. Dependence of the Productivity on the Method of Raw Material Processing. *Bioorg. Chem.* **2020,** *99*, 103773.

[130] Adamu, M.; Ibrahim, Y.E.; Alanazi, H. Optimization of Sustainable Concrete Properties Modified with Blends of Date Palm Ash and Eggshell Powder Using Response Surface Methodology. *Develop. Built Environ.* **2024,** 100359. https://doi.org/10.1016/j.dibe.2024.100359.
[131] Adeoye, A.O.; Quadri, R.O.; Lawal, O.S.; Emojevu, E.O. Physicochemical Characterization, Valorization of Lignocellulosic Waste (Kola Nut Seed Shell) via Pyrolysis, and Ultrasonication of its Crude Bio-Oil for Biofuel Production. *Cleaner Waste Syst.* **2024,** 100138. https://doi.org/10.1016/j.clwas.2024.100138.
[132] Olubajo, O.O.; Odey, O.A.; Abdullahi, B. Potential of Orange Peel Ash as a Cement Replacement Material. *Traektoriâ Nauki = Path Sci.* **2019,** *5* (7), 2009–2019.
[133] Pa, F.C.; Abdullah, C.; Fazlul, B. Review of Extraction of Silica from Agricultural Wastes Using Acid Leaching Treatment. *Adv. Mat. Res.* **2013,** *626*, 997–1000.
[134] Uchegbulam, I.; Momoh, E.O.; Agan, S.A. Potentials of Palm Kernel Shell Derivatives: A Critical Review on Waste Recovery for Environmental Sustainability. *Cleaner Mater.* **2022,** *6*, 100154. https://doi.org/10.1016/j.clema.2022.100154.
[135] Flores, C.G.; Schneider, H.; Dornelles, J.S.; Gomes, L.B.; Marcilio, N.R.; Melo, P.J. Synthesis of Potassium Zeolite from Rice Husk Ash as a Silicon Source. *Cleaner Eng. Technol.* **2021,** *4*, 100201. https://doi.org/10.1016/j.clet.2021.100201.
[136] Ogwang, G.; Olupot, P.; Kasedde, H.; Menya, E.; Storz, H.; Kiros, Y. Experimental Evaluation of Rice Husk Ash for Applications in Geopolymer Mortars. *J. Bioresour. Bioproducts* **2021,** *6* (2), 160–167.
[137] De Silva, G.S.; Aagani, T.; Gebremariam, K.F.; Samarakoon, S.S.M. Engineering Properties and Microstructure of a Sustainable Roof Tile Manufactured with Waste Rice Husk Ash and Ceramic Sludge Addition. *Case Stud. Construct. Mater.* **2022**, *17*, e01470.
[138] Kirthiga, R.; Elavenil, S. Potential Utilization of Sugarcane Bagasse Ash in Cementitious Composites for Developing Inorganic Binder. *Ain Shams Eng. J.* **2023,** *14* (11), 102560.
[139] Patel, K.G.; Shettigar, R.R.; Misra, N.M. Recent Advance in Silica Production Technologies from Agricultural Waste Stream. *J. Adv. Agricul. Technol.* **2017,** *4* (3), 274–279.
[140] Kavaz, D.; Vaseashta, A. Synthesizing Nano Silica Nanoparticles from Barley Grain Waste: Effect of Temperature on Mechanical Properties. *Pol. J. Environ. Stud.* **2019,** *28* (4), 1–9.
[141] Ananthi, A.; Geetha, D.; Ramesh, P. Synthesis and Characterization of Silica from Ragi Husk Ash (Finger Millet) by a Sol-Gel Method. *Synthesis (Mass)* **2017,** *9* (3), 61–65.
[142] Saed, B.; Ziaee, M.; Kiasat, A.R.; Jafari nasab, M. Preparation of Nanosilica from Sugarcane Bagasse Ash for Enhanced Insecticidal Activity of Diatomaceous Earth Against Two Stored-Products Insect Pests. *Toxin. Rev.* **2022,** *41* (2), 516–522.
[143] Morales-Paredes, C.A.; Rodríguez-Linzán, I.; Saquete, M.D.; Luque, R.; Osman, S.M.; Boluda-Botella, N.; Manuel, R.-D.J. Silica-Derived Materials from Agro-Industrial Waste Biomass: Characterization and Comparative Studies. *Environ. Res.* **2023,** *231*, 116002. https://doi.org/10.1016/j.envres.2023.116002.
[144] Younes, N.A.; El-Sherbiny, M.; Alkharpotly, A.; Sayed, O.; Dawood, A.F.; Hossain, M.A.; Abdelrhim, A.S.; Dawood, M.F. Rice-Husks Synthesized-Silica Nanoparticles Modulate Silicon Content, Ionic Homeostasis, and Antioxidants Defense Under Limited Irrigation Regime in Eggplants. *Plant Stress* **2024,** *11*, 100330.
[145] Adam, F.; Chew, T.-S.; Andas, J. A Simple Template-Free Sol–Gel Synthesis of Spherical Nanosilica from Agricultural Biomass. *J. Sol-Gel Sci. Technol.* **2011,** *59*, 580–583.
[146] Wang, W.; Martin, J.C.; Fan, X.; Han, A.; Luo, Z.; Sun, L. Silica Nanoparticles and Frameworks from Rice Husk Biomass. *ACS Appl. Mater. Interfaces* **2012,** *4* (2), 977–981.
[147] Hassan, A.; Abdelghny, A.; Elhadidy, H.; Youssef, A. Synthesis and Characterization of High Surface Area Nanosilica from Rice Husk Ash by Surfactant-Free Sol–Gel Method. *J. Sol-Gel Sci. Technol.* **2014,** *69*, 465–472.
[148] Hu, S.; Hsieh, Y.-L. Preparation of Activated Carbon and Silica Particles from Rice Straw. *ACS Sustain. Chem. Eng.* **2014,** *2* (4), 726–734.
[149] Palanivelu, R.; Manivasakan, P.; Dhineshbabu, N.; Rajendran, V. Comparative Study on Isolation and Characterization of Amorphous Silica Nanoparticles from Different Grades of Rice Hulls. *Synth. React. Inorg., Met.-Org., Nano-Met. Chem.* **2016,** *46* (3), 445–452.
[150] Imoisili, P.E.; Ukoba, K.O.; Jen, T.-C. Green Technology Extraction and Characterisation of Silica Nanoparticles from Palm Kernel Shell Ash Via Sol–Gel. *J. Mater. Res. Technol.* **2020,** *9* (1), 307–313.
[151] Dorairaj, D.; Govender, N.; Zakaria, S.; Wickneswari, R. Green Synthesis and Characterization of UKMRC-8 Rice Husk-Derived Mesoporous Silica Nanoparticle for Agricultural Application. *Sci. Rep.* **2022,** *12* (1), 20162. https://doi.org/10.1038/s41598-022-24484-z.
[152] Tessema, B.; Gonfa, G.; Mekuria Hailegiorgis, S.; Venkatesa Prabhu, S. An Overview of Current and Prognostic Trends on Synthesis, Characterization, and Applications of Biobased Silica. *Adv. Mater. Sci. Eng.* **2023,** *2023*. https://doi.org/10.1155/2023/4865273.
[153] Silviana, S., Saputra, B., Oktavian, H.D.A., Arrois, S., Agung, G.W., Situmorang, B., Dewanti, A.M.D., Mustofa, C., Saputra, R.F.A.; Tristanto, V. F. (2024). Rice Husk as a Potential Source for the Sol-Gel Synthesis of Diphenylcarbazide Immobilized Silica Adsorbent for the Adsorption of Lead. AIP Conference Proceedings
[154] Vu, A.-T.; Nguyen, M.V.; Nguyen, T.H. Fabrication of Ethylenediaminetetraacetic Modified Porous Silica Composite from Rice Husk for Enhancing the Remove of Pb2+ from Aqueous Solution. *Results Mater.* **2024,** *21*, 100525. https://doi.org/10.1016/j.rinma.2023.100525.
[155] Asgharinezhad, A.A.; Esmaeilpour, M.; Afshar, M.G. Synthesis of Magnetic Fe3O4@ SiO2 Nanoparticles Decorated with Polyvinyl Alcohol for Cu (II) and Cd (II) Ions Removal from Aqueous Solution. *Chem. Pap.* **2024,** *78*, 1–16.
[156] Santhamoorthy, M.; Thirumalai, D.; Thirupathi, K.; Kim, S.-C. Synthesis of Dithiol-Modified Mesoporous Silica Adsorbent for Selective Adsorption of Mercury Ions from Wastewater. *Appl. Nanosci.* **2023,** *13* (9), 6015–6024.

[157] Al-Wasidi, A.S.; Katouah, H.A.; Saad, F.A.; Abdelrahman, E.A. Functionalization of Silica Nanoparticles by 5-Chloro-8-Quinolinol as a New Nanocomposite for the Efficient Removal and Preconcentration of Al3 + Ions from Water Samples. *ACS Omega* **2023,** *8* (17), 15276–15287.
[158] Flores, D.; Almeida, C.M.R.; Gomes, C.R.; Balula, S.S.; Granadeiro, C.M. Tailoring of Mesoporous Silica-Based Materials for Enhanced Water Pollutants Removal. *Molecules* **2023,** *28* (10), 4038. https://doi.org/10.3390/molecules28104038.
[159] Purrostam, S.; Rahimi-Ahar, Z.; Babapoor, A.; Nematollahzadeh, A.; Salahshoori, I.; Seyfaee, A. Melamine Functionalized Mesoporous Silica SBA-15 for Separation of Chromium (VI) from Wastewater. *Mater. Chem. Phys.* **2023,** *307*, 128240. https://doi.org/10.1016/j.matchemphys.2023.128240.
[160] sadat Hashami, Z.; Taheri, A.; Alikarami, M. Synthesis of a Magnetic SBA-15-NH2@ Dual-Template Imprinted Polymer for Solid Phase Extraction and Determination of Pb and Cd in Vegetables; Box Behnken Design. *Anal. Chim. Acta* **2022,** *1204*, 339262. https://doi.org/10.1016/j.aca.2021.339262.
[161] Xing, Y.; Li, Q.; Chen, X.; Li, M.; Wang, S.; Li, Y.; Wang, T.; Sun, X.; Li, X. Preparation of Isoelectric Point-Switchable Polymer Brush-Grafted Mesoporous Silica Using RAFT Polymerization with High Performance for Ni (II) Adsorption. *Powder Technol.* **2022,** *412*, 117980. https://doi.org/10.1016/j.powtec.2022.117980.
[162] Abukhadra, M.R.; Eid, M.H.; El-Meligy, M.A.; Sharaf, M.; Soliman, A.T. Insight Into Chitosan/Mesoporous Silica Nanocomposites as Eco-Friendly Adsorbent for Enhanced Retention of U (VI) and Sr (II) from Aqueous Solutions and Real Water. *Int. J. Biol. Macromol.* **2021,** *173*, 435–444.
[163] Jumah, M.N.B.; Eid, M.H.; AL-Huqail, A.A.; Mohammad, M.A.; Bin-Murdhi, N.S.; Abu-Taweel, G.M.; Altoom, N.; Allam, A.A.; AbuKhadra, M.R.. Enhanced remediation of As (V) and Hg (II) ions from aqueous environments using β-cyclodextrin/MCM-48 composite: Batch and column studies. *J. Water Process Eng.*. **2022**, *42*, 102118.
[164] Sethy, T.R.; Sahoo, P.K. Highly Toxic Cr (VI) Adsorption by (Chitosan-g-PMMA)/Silica Bionanocomposite Prepared Via Emulsifier-Free Emulsion Polymerisation. *Int. J. Biol. Macromol.* **2019,** *122*, 1184–1190.
[165] Soltani, R.; Dinari, M.; Mohammadnezhad, G. Ultrasonic-Assisted Synthesis of Novel Nanocomposite of Poly (Vinyl Alcohol) and Amino-Modified MCM-41: A Green Adsorbent for Cd (II) Removal. *Ultrason. Sonochem.* **2018,** *40*, 533–542.
[166] Nasreen, S.; Urooj, A.; Rafique, U.; Ehrman, S. Functionalized Mesoporous Silica: Absorbents for Water Purification. *Desalin. Water Treat.* **2016,** *57* (60), 29352–29362.
[167] Lee, J.-Y.; Chen, C.-H.; Cheng, S.; Li, H.-Y. Adsorption of Pb (II) and Cu (II) Metal Ions on Functionalized Large-Pore Mesoporous Silica. *Int. J. Environ. Sci. Technol.* **2016,** *13*, 65–76.
[168] Wongsakulphasatch, S.; Kiatkittipong, W.; Saiswat, J.; Oonkhanond, B.; Striolo, A.; Assabumrungrat, S. The Adsorption Aspect of Cu2+ and Zn2+ on MCM-41 and SDS-Modified MCM-41. *Inorg. Chem. Commun.* **2014,** *46*, 301–304.
[169] Sharififard, H.; Rezvanpanah, E. Ultrasonic-Assisted Synthesis of SiO 2 Nanoparticles and SiO 2/Chitosan/Fe Nanocomposite and Their Application for Vanadium Adsorption from Aqueous Solution. *Environ. Sci. Pollut. Res.* **2021,** *28*, 11586–11597.