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Recent development in metal-doped SBA-15 catalyst for heterogeneous catalysis and sustainable chemistry: a mini-review.

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Abstract

For the invention of new advanced sustainable materials for heterogeneous catalysis require control of structural parameter of active sites. Mesoporous silica, especially SBA-15 has some unique and important features such as highly ordered mesopore, greater hydrothermal stability, greater wall thickness, large surface area, and adjustable pore volume. All these properties render it a promising material for catalysis, adsorption, supporting material, biomedical application, and environmental remediation. However, purely SBA-15 lacks acidic characters, which hinder its catalysis capabilities. Therefore, functionalized SBA-15 improves the catalytic activities for versatile applications. Thus, in this paper, we attempted to summarize the synthesis procedures, various functionalization processes, and application of metal modified SBA-15 in organic synthesis, fine chemical synthesis, photocatalysis, and decontamination of water. Furthermore, physicochemical properties, sustainability, and efficacies are discussed in detail for future reference and scope of studies.

Keywords: Nanocomposite, metal substituted SBA-15, Organic Transformation, Environmental Application.

1. Introduction

Mesoporous materials, as classified by IUPAC nomenclature, are porous materials whose pore size range from 2-50 nm. Mesoporous silica has been a popular class of 2D ordered materials to study since its discovery in 1990 at Mobil Corporation, USA. MCM-41 and SBA-15 are the two main types of mesoporous silica. These materials attracted the attention of the researcher for their number of unique properties including, larger surface area, highly ordered mesochannel, adjustable pore volume, accessibility, which allows homogeneous diffusion and adsorption of large molecules for versatile application. In 1992, MCM-41 was discovered in the same laboratory and identified some unique properties, which are high surface area ($>800 \text{ m}^2/\text{g}$), well-defined pore, consistent pore size distribution, and adjustable pore diameter ($\sim 10 \text{ nm}$). Six years later, in 1998, Zhao et.al discovered Santa Barbara Amorphous (SBA-15) materials at the University of California, USA. The SBA-15 was found to possess more improved qualities in physicochemical properties. The outstanding properties of SBA-15 are larger surface area ($600\text{--}1000 \text{ m}^2/\text{g}$), large pore volume ($\sim 2.5 \text{ cm}^3/\text{g}$), tunable pore diameter (2-50nm), and greater wall thickness ($\sim 30 \text{ \AA}$), which provides greater hydrothermal stability ($\sim 800 \text{ }^\circ\text{C}$) than MCM-41. Besides, cylindrical and parallel mesopores of SBA-15 allow considerable accessibility for

homogeneous distribution of active phases in catalyst and easy diffusion of reactant. Owing to these characteristics, SBA-15 acts as an outstanding catalyst and catalyst support for a variety of applications.

Although pure SBA-15 has several advantages, it also has certain drawbacks such as lower surface acidity, which makes it inappropriate for a variety of reactions. The SBA-15 materials can be functionalized with a suitable metal, metal oxide, or functional group to overcome this constraint. As a result, as compared to bare SBA-15, the functionalized SBA-15 shows higher catalytic activity. Furthermore, the mesopore channel provides space for smooth and equal distribution of functional groups. So far, there is only a little review paper on functionalized SBA-15 available in open source with limited focus on applications such as catalysis, Friedel craft reaction, organic synthesis, and biorefinery application [4-8]. In this review, we focused our study on the synthesis method of various metal and metal oxide functionalized SBA-15 and their application in organic synthesis, syn-gas synthesis, oxidation reaction, reduction reaction, cycloaddition reaction, photocatalysis, and removal of pollutant from water bodies. Moreover, the efficiency, sustainability, and morphologies are discussed for future reference.

2. Synthesis Procedure

The original fabrication method of SBA-15 synthesis is a hydrothermal method using surfactants Pluronic (P123) as structure-directing agents, as described by Zhao et.al [1]. A typical synthesis procedure (Figure-1) includes the following steps: (a) dissolution of amphiphilic triblock copolymer at low temperature ($\sim 40^{\circ}\text{C}$) in acidic medium, (b) addition of silica source at same condition and aging for 24h, (c) hydrothermal treatment at $80\text{-}100^{\circ}\text{C}$ for 48h, (d) Cooling, filtration, washing & drying, and last step (e) calcination at $500\text{-}550^{\circ}\text{C}$ for 5h. Tetraethyl orthosilicate (TEOS) is the most preferred silica source, as it produces highly pure SBA-15 material with excellent morphology. Moreover, for structure agent, surfactant Pluronic, P123, ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$) copolymer is used owing to the low cost, biodegradability, availability and to get the desired structure of SBA-15.

Figure-1. A typical synthesis steps of SBA-15

Various synthesis procedures have been employed, which include direct synthesis, post-synthetic wet impregnation, Sonication, post-grafting, Insitu-method, the chemical fluid method, evaporation induced wet impregnation, as well as immobilization [38-45]. Table-1 illustrates the different types of synthesis of functionalized metal-doped SBA-15 and their textural properties. However, only direct synthesis and wet incipient impregnation methods will be discussed in this review.

2.1 Direct method:

The direct method of functionalized SBA-15 involves co-condensation of silica sources such as TEOS, TMOS, etc. with organotrialkoxysilane in the presence of templating agents. It was then further extended to co-condensing silica sources with various metals such as transition metal, alkaline metal, rare earth metal, and metalloid. The direct method facilitates the isomorphous substitution of heteroatoms in the mesoporous silica via co-condensation and is normally carried out in an acidic medium. However, recent developments suggest that it can be carried out at neutral conditions by using hydroxyl radical [32]. Furthermore, direct synthesis suggests a uniform distribution of functional groups on the SBA-15 material surface and structure, preserving the morphology of materials which is in accordance with the finding of Zhao et al [1]. Table-1 demonstrates the different metal-doped SBA-15 synthesized by direct, post grafting, wet impregnation, and others methods with their obtained textural properties. It can be seen that the direct method provides excellent physicochemical properties to the catalyst.

Table-1 Different types and modified metal-doped SBA-15

Catalyst	Method	Textural Properties			Application	Reference
		BET	Vp	Dp(nm)		
Cu/SBA-15	Direct method (hydrothermal)	855	1.35	6.53	Ethanol oxidation	27
Sn/SBA-15	Direct method	690	1.06	6.83	Ethanol oxidation	27
Cu/SBA-15	Direct method	733	1.59	9.3	Oxidative degradation of MO	32
Zr/SBA-15 (10)	Direct method	645	-	7.48	Furfural to methyl levulinate	52
Zr/SBA-15	Hydrothermal, Hydrolysis method	348.69	0.38	-	Conversion of Benzyl alcohol to Benzaldehyde	30
Ni-AlSBA-15	Hydrothermal, Wet Impregnation	567	0.87	6.5	Dry reforming of methane	18
Cu-SBA-15/SO ₃ H	Hydrothermal, Post grafting	433.2	0.56	4.1	Conversion of Xylose to Furfuryl alcohol	34
Ru-Zr-AlSBA-15	Hydrothermal, Insitu Method,& Wet	840	1.64	6.51	Conversion of Lenuvic acid to 2-methyl	38

Ru ₅ -Al ₂₀ - SBA-15	Impregnation Hydrothermal, Chemical Fluid deposition (CFD)	622	0.77	5.6	tetrahydrofuran Hydrogenation of dimethyl terephthalate to 1,4- cyclohexane carboxylate	43
Cu-Zr/SBA-15	Hydrothermal, Evaporation induced wet impregnation	316	0.8	13	Hydrogenation of CO ₂ to methanol	45
CuO-ZnO- ZrO ₂ /SBA-15	Hydrothermal, Wet impregnation	387.6	0.54	5.57	Hydrogenation of CO ₂ to methanol	47
Ni-Pd/SBA-15	Hydrothermal, wet impregnation	541	1.19	6.65	Conversion of CO ₂ to methane	49
Ni-Co/SBA-15	Hydrothermal, Wet impregnation	386.7	1.11	7.61	Hydrogenation of furfural to tetrahydro furfuryl alcohol	53
Fe ₃ O ₄ @WO ₃ /SBA- 15	Hydrothermal, wet impregnation	410.4	0.63	6.48	Photocatalysis	54

2.2 Wet impregnation

The wet impregnation method is the most commonly post grafting technique employed to doped different metal or metal oxide to the mesopore channel of SBA-15. Typically, a soluble salt of metal was dissolved in water or solvent, and then a calculated amount of previously prepared SBA-15 been added to the solution. Agitating the suspension for a certain period, followed by separation and drying was done to get the metal-doped SBA-15. The obtained powder is preferably calcined at a muffle furnace to get metal oxide doped SBA-15. This method has been employed in different metal loading in SBA-15 as it is very simple, economic, and easy to work up. Additionally, it does not require a sophisticated instrument. The only drawback of this method is the lower textural properties of metal-doped SBA-15 compare to the direct synthesis method, as can be seen in Table-1. Notably, wet impregnation methods do not alter the geometrical structure (2D hexagonal) and remain similar to bare SBA-15 [11, 47].

3. Recent advances in synthetic chemistry by metal-doped SBA-15 nanocomposite.

3.1 One-pot synthesis for organic transformation.

The one-pot synthesis technique is usually a paramount step forward for the green chemistry principle. The principle is extensively applied to organic transformation reactions by various enterprises where Active pharmaceutical ingredients (API), drug synthesis, especially Biopharma, generic sector, and chemical industries where synthetic chemistry is used. Recently, Dido CA et.al reported SBA-15/AuNP composite as a heterogeneous catalyst for the synthesis of 2-aryl-2, 3-dihydro quinazoline-4 (1H)-ones (DHQ) from 2-aminobenzamide and benzaldehyde (R-CHO) as depicted in scheme-1^[9]. The author describes for the first time the use of Lewis acid sites present in gold nanoparticles anchored in cylindrical pores of SBA-15. With 30mg catalyst (0.6% Au Mol), the obtained yield was 91 % and a series of different substituted aromatic aldehyde (R-group) was studied to test the efficacy of conversion. The author also found the electron-withdrawing group and electron-donating group has less effect and the reaction proceeds smoothly. Another important one-pot synthesis reaction is the Biginelli condensation reaction (Scheme-2) in the production of dihydro-pyrimidinone (DHPM) derivatives. Bhuyan et al reported the ZnO/SBA-15 catalyst for this transformation reaction. However, Mahato, BN et.al reported the ZnO/Al-SBA-15 catalyst as superior, efficient with 98 % yield at a lower temperature, and a short time making the reaction greener ^[11].

Scheme-1, Synthesis of Dihydroquinazolinone

Scheme-2 Biginelli Condensation Reaction

3.2 Suzuki coupling

The Suzuki coupling reaction is well known for the construction of the C-C bond in synthetic chemistry (scheme-3). An aryl-aryl bond, alkyl-aryl, and alkyl-alkyl bond could be built with selective chirality by using the Suzuki coupling. Recently, Li et al reported a green synthesis method for Pd NR/ SBA-15 catalyst and employed it in the Suzuki coupling reaction between phenylboronic acid and 4-bromotoluene ^[12]. The silent feature of this work includes the palladium nanorods incorporation onto mesoporous SBA-15 via in-situ reduction induced from the ultrasonic process. The obtained yield was 96.4 %. Furthermore, the coupling reaction occurs smoothly for *p*- substituted aryl halide containing either electron-withdrawing or electron-donating groups. However, the author reported steric-effect hinders the yield of the product. Besides, the yield of the product was 90.6% in the 5th run on the recyclability test of catalyst.

Scheme-3 Suzuki Coupling

3.3 Cyanation

The fabrication of the C-N bond in organic synthesis is used to make bioactive and drug intermediate compounds. Chang et.al has worked significantly in aryl cyanation reaction; however, in recent work, Boos et.al reported the Cu/SBA-15 catalyst is highly selective in the C₃-cyanation of indole by using cyanating agent as NH₄I and DMF^[15]. Notably, O₂ from the air source is used as an oxidant. The 10% wt Cu/SBA-15 catalyst shows a superior yield of 92 % in comparison to other metals such as Ni, Pd, and Ru doped SBA-15 catalysts. The reaction proceeds through electrophilic aromatic substitution (iodination) followed by cyanation.

Scheme-4 Cyanation of methyl Indole

3.4 Syn-gas synthesis

A mixture of CO and H₂O commonly termed Syn-gas, is primarily produced via a fascinating reaction known as a Dry reforming reaction. It utilizes two greenhouse gases CO₂ and CH₄ and produces H₂ in a greener way. These two gases are major contributors to global warming leading to climate changes worldwide [16]. Therefore, it is very useful to modern society to convert the gases into a value-added product. In this context, the dry reforming reaction holds a pivotal role in petrochemical industries. Furthermore, the catalyst used for this reaction is mainly two classes; Ni-based and noble metal-based. Despite coke formation of nickel-based catalyst, it is the most preferable choice for industries owing to low cost, high abundance, and recyclability. However, coke formation on the nickel can be circumvented by dispersing the metal in suitable support usually SBA-15 [17-20]. Recently, Abdullah et.al reported Ni/SBA-15 catalysts for syn-gas production [21]. The highlights of this work include a novel method of SBA-15 synthesis using palm oil, fuel ash silica precursor and has extensively studied the effect of different what % of Ni incorporation on the reaction.

Scheme-5, Syn-Gas Synthesis

3.5 Cycloaddition

CO₂ Cycloaddition is a promising strategy between CO₂ and epoxied to produce five-membered cyclic carbonate and polycarbonate. Polycarbonates are used electrolytes in Li-ion batteries,

polar aprotic solvent, polymer production, Fine chemicals, and intermediates [23]. Therefore, valorization of CO₂ and mitigation of the greenhouse effect (due to CO₂) make the reaction imperative. So far the reaction is predominantly catalyzed by metal salt of Cu, Pd, and Zn. Furthermore, the synergistic effect in the catalyst can be induced by adding a nucleophile functional group along with acidic sites [22, 24]. More recently, Jayakumar, S, and co-worker reported bifunctional Zn-Tpy/SBA-15 composite catalyst for the CO₂ cycloaddition reaction. The catalyst has a synergistic effect with a high turnover frequency (TOF) value of 1686 h⁻¹ suggesting an efficient catalyst [25].

Scheme-6. Cycloaddition Reaction

3.6 Fine chemicals

The oxidation of various chemicals and chemical intermediates obtained as byproducts in various chemical processes are of much importance to get usable products. Thus, it offers the atom economy and environmental compatibility. For example, converting benzyl alcohol, ethanol, glycerol, and propane to value-added products like benzaldehyde, acetaldehyde, carboxylic acids, and acrolein respectively, are very important as these chemicals are prepared via renewable resources and find extensive application [26-29]. Recently, these products have had high market demands. For these conversion processes, heterogeneous catalysts mainly noble or transition metal and metal oxide are used. However, normally metals or metal oxides are expensive and possess a low surface area, therefore it is a rational strategy that dispersing them on suitable support will make them cheaper, more accessible, and recyclable. Recently, Li et. al,

has prepared magnetic Pd/Co- SBA-15 and applied it to liquid phase oxidation of benzyl alcohol to benzaldehyde [26]. The author reported selectivity of 83.2 % at the milder condition in solvent-free condition. The silent feature of this work is the synergistic and promotional effect of cobalt in the conversion process. This fact has been established by comparing with Pd/Mn-SBA-15, Pd/Cu-SBA-15, and Pd/Zn- SBA-15 catalysts. Another prominent work for this conversion is by catalysts Zirconium oxide doped SBA-15 (ZrO₂/SBA-15) [30]. The author reported 97% selectivity of benzaldehyde as a major product with 97 % conversion with TOF ~ 18.03 s⁻¹. The reaction was conducted at 90°C and tertiary butyl hydrogen peroxide as oxidants. Similarly, Akti et.al has studied ethanol oxidation to acetaldehyde by the catalyst Sn/Cu-SBA-15 [27]. The acetaldehyde selectivity of 58% and conversion of 95% were noted at temperature 300°C. The glycerol oxidation to the carboxylic acid by Pt/MgO-SBA-15 in a base-free medium has been reported by Yan et.al in 2019 [54]. The salient feature of this catalyst is the selectivity of C₃ value-added products such as glyceric acid, glyceraldehydes, and dihydroxyacetone is excellent in comparison to other heterogeneous catalysts. The brilliant TOF value of 1672.2 h⁻¹ was reported. Furthermore, the synergistic role of MgO i.e. reduction of C-H bonds and activation of O-H bonds is confirmed by DFT calculation.

Table-2 Different metal functionalized SBA-15 for various chemical reactions.

Catalyst	Product	Yield %	selectivity	TOF	Recycl ability	Ref.
AuNP/SBA-15	2-phenyl-2,3-dihydroquinazolin-4(1H)-one	91	-	-	-	9
ZnO NP/SBA-15	Dihydropyrimidinone(DHPM) derivatives	76-96	-	-	4	10
ZnO/AlSBA-15	DHPM	98	-	-	4	11
Pd-me_Im/SBA-15	Biphenyl	99	-	-	4	13
Cu-creatinine-SBA-15	Diphenyl disulfide derivatives	91-96	-	-	4	14
Cu-SBA-15	Indole derivative	65-92	-	-	4	15
Pd-Zn-SBA-15	Benzyl alcohol to benzaldehyde	95	80		5	26

Zr-SBA-15	Benzyl alcohol to Benzaldehyde	96	100	18.21 s ⁻¹	5	30
Pt-MgO-SBA-15	Glycerol oxidation to glyceric acid	60.2	65.5	1671.2 h ⁻¹	-	31
Ru ₅ -Al ₂₀ -SBA-15	Dimethyl terephthalate to dimethyl cyclohexanedicarboxylate	93.4	100	-	5	43
Pd-In ₂ O ₃ -SBA-15	CO ₂ Hydrogenation to methanol		83.9	-	-	48
Ni-Pd-SBA-15	CO ₂ methanation	93.7	96.1	-	-	49
Al ₂ O ₃ -SBA-15	Conversion of fructose into ethyl levulinate	58	86	-	-	51
Zr-SBA-15	Conversion of furfural to methyl levulinate	36.3	100	-	5	52

3.7 Biomass valorization

Biomass valorization is a promising, advanced technology, suitable approach as it offers great potential for the conversion of waste to value-added product. The lignocellulosic waste biomass, waste food, oil, and non-edible plant component can be converted into bio-fuel. Biomass-derived furfural such as furfuryl alcohol, methyl levulinate, Maleic anhydride, succinic acid, and many more chemicals intermediate is prepared by renewable resources. These chemicals find extensively used for the synthesis of the valuable compound for flavoring agents, fuel additives, and fine chemicals [36-53]. In recent times, Fang et al have been studied the catalytic conversion of methyl levulinate to γ -valeroacetone (GVL). The author fabricated the Cu-Ni/SBA-15 catalyst and reported high activity, stability, and 91.3% conversion of methyl levulinate with 89.7 % selectivity of GVL at 140°C in 3h. The prominent feature of this catalyst is a superb transfer hydrogenation reaction. A similar type of work has performed by kondeboina et.al in 2018. However, the author invented continuous production of GVL, and reported the 77% yield of GVL in the 24h stream by using Co-SBA-15 catalyst under atmospheric H₂ pressure [36-38].

Hydrogenation of Carbon dioxide into methanol is believed to be an important reaction as it mitigates the greenhouse effect. Noble metals such as Pd, Ni, etc. are used to catalyze the CO₂

hydrogenation process. The selective hydrogenation of CO₂ gives the product methane, methanol as shown in equations (1) and (3) respectively.

Recently, Jiang et.al has reported an efficient Pd/In₂O₃/SBA-15 catalyst for selective conversion of CO₂ to methanol. The catalyst shows an excellent synergistic effect along with 89.3% methanol selectivity and 12.6 % CO₂ conversion at 5 Mpa pressure and temperature 260°C. The Pd functional help in dissociation of H₂ and In₂O₃ promotes the CO₂ conversion [71].

4. Photocatalysis

Photocatalysis is an emerging technology in which solar energy is converted to chemical energy. It's noteworthy to mention here that the photocatalyst does not change chemically during or after the reaction. The terms "photocatalyst" and "catalyst" are frequently interchanged in the literature. It's most likely explained by the fact that photocatalytic materials are occasionally used as catalysts in catalytic reactions. However, the concepts of catalysis and photocatalysis differ in terms of thermodynamics. Photocatalysis can thus drive energy-storing processes (DG>0), whereas catalysis is limited to thermodynamically feasible reactions (DG<0). Photocatalytic activity refers to the rate of reaction (absolute or relative) in a photocatalytic process. The widely known hypothesis can be used to describe the main concept of photocatalysis. When photocatalytic material is subjected to light with energy equal to or greater than the bandgap of the photocatalyst, electron-hole pairs are formed. In the conduction band, formed electron-hole pairs disintegrate into electrons (e) and holes (h) in the valence band. The 'e' and 'h' cause molecules adsorbing on a photocatalytic material's surface to be reduced and oxidized. Nonetheless, electron-hole recombination occurs often, which may prevent oxidation and reduction reactions from occurring on the surface of photocatalytic materials. An augmented or suppressed electrification is frequently linked to an increase or decrease in reaction rate.

Several semiconducting metals, alloy, and metal oxide nanostructure supported on SBA-15 material employed for this purpose owing to the suitable energy gap (E_g). However, TiO₂ based

material is most preferred and studied for this purpose due to its self-cleaning effect, stability, non-toxic, and excellent photocatalytic activity by generating a sizable number of electrons and holes upon irradiation [68]. While the Bandgap of anatase-TiO₂ (E_g=3.2 eV) phase is higher than rutile-TiO₂ (E_g = 2.8 eV) can be activated by UV irradiation ($\lambda < 387$ nm). Furthermore, the magnetically separable material has great attention in research due to its easy separation. Therefore, it is indeed to have a magnetic photocatalyst that would claim to be an ideal candidate. In this context, thanks to colloid chemistry for capable of synthesizing a broad range of materials of choice. A Core-shell structure is one such type of material with adjustable morphologies. Recently, Lima MS and co-worker reported Fe₃O₄@WO₃/SBA-15 as an efficient and magnetically separable photocatalyst for photodegradation of dichlorophenoxy acetic acid [54]. The prominent feature of catalyst is the core-shell structure of magnetite-tungsten oxide embedded in the mesopores of SBA-15. WO₃ generates photoelectron which is subsequently accepted at Fe₂O₃ leading to the formation of O₂⁻ radical by suppressing the O₂ in solution.

Table-3 Different metal functionalized SBA-15 as photocatalyst

Photocatalyst	Band gap (Ev)	BET (m2/g)	pollutant	Conc. (ppm)	pH	Reaction time (min)	Removal %	Ref.
NiFe700/SBA-15	2.09	554	Carbendazin	20	2	1400	33.3	57
CoFe700/SBA-15	2.20	574	Carbendazin	20	2	1400	96.0	57
41% TiO ₂ /SBA-15		505.4	Methylene Blue	30	-	150	85.0	60
Nd-TiO ₂ /SBA-15	-	8	Methylene Blue	-	4	140	94.1	61
TiO ₂ /SBA-15	3.41	369.9	Rhodamine B	-	4.5	150	-	62
Sn _{0.05} Ti _{0.95} O ₂ -SBA-15	3.37	369.9	Rhodamine B	-	4.5	150	-	62

Sn _{0.08} Ti _{0.92} O ₂ - SBA-15	3.32	373.7	Rhodamine B	-	4.5	150	-	62
SnO ₂ -SBA-15	3.77	318.7	Rhodamine B	-	4.5	150	-	62
26% TiO ₂ - SBA-15		686	Dimethoate	30	12	420	Complete degradation	63
TiO ₂ -SBA-15	3.30	587	Methylene Blue	20	-	-	97	64
ZnO/SBA-15	4.01	399	Methylene Blue	20	-	-	95	64
SnO ₂ /SBA-15	4.06	564	Methylene Blue	20	-	-	86	64
Ag ₃ PO ₄ /SBA-15 (20%)	2.14	373.3	Ciprofloxacin	10	-	210	61.96	65
CdS/SBA-15		186	Salicylic Acid	10	-	360	84.93	66

Scheme-7 General procedure of Photocatalysis (inset fig. - mechanism of photocatalysis).

5. Adsorption

Now a day's, the drinking water crisis is a major concern worldwide owing to the rise in population and industrialization. Inorganic and organic soluble compounds are responsible for water pollution. The insecticide, herbicide, and dyes contain organic pollutants which affect our health and ecosystem. Furthermore, heavy metal elements such as Pb, Cd, As, Cr, etc. are hazardous, carcinogenic to our health at a minuscule level [69-75]. The heavy metal comes into water bodies via human activity, mining, and industrial activity. Therefore, the significance of the removal of hazardous pollutants is a prime concern in modern society. There are many technologies available for the removal of heavy metal, but adsorption is a simple, low-cost, easy to work up, and cost-effective method. Peng and co-workers have contributed several studies on heavy metal removal from water bodies. Notably, one such kind of work is $\gamma\text{-Fe}_2\text{O}_3/\text{SBA-15}$ adsorbent for Arsenic removal [74]. The prominent features of adsorbent are; magnetically separable, recyclable, and regeneration by NaOH. The magnetic saturation of 6.23emu/g was measured for this adsorbent.

Toxic Organic pollutants such as carbamazepine, clofibric acid, salicylic acid, methylene blue, acid blue-25, Rhodamine, and many more are the byproduct of pharmaceutical, dyes, textile, and chemical industries. These substances heavily degraded the quality of water and were unfit for domestic use. Therefore, the pollutant must be removed from the water system for re-use of water. Recently, Ghanei et al prepared a magnetic-SBA/15 CPAA nanocomposite and applied it to the adsorption of Acid Blue 25. The author found the magnetic saturation of 2.683 emu/g and the maximum adsorption capacity of 909.09 mg g⁻¹ [70]. This apart, the adsorbent is easily separated by the simple magnet, which makes the process very convenient. Table-4 illustrates the permissible limits of various pollutants by the different regulator and Table-5 list down the functionalized SBA-15 materials for removal of pollutants.

Table-4 Permissible limits of drinking water.

Parameter	USEPA	WHO	ISI	ICMR	CPCB
pH (mg/l)	6.5-8.5	6.5-8.5	6.5-8.5	6.5-9.2	6.5-8.5
Turbidity NTU	-	-	10	25	10
Conductivity(mg/l)	-	-	-	-	2000
Alkalinity(mg/l)	-	-	-	-	600
Total Hardness(mg/l)	-	500	300	600	600
Iron (mg/l)	-	0.1	0.3	1.0	1.0
Chloride (mg/l)	250	200	250	1000	1000
Copper (mg/l)	1.3	1.0	0.05	1.5	1.5
Mercury (mg/l)	0.002	0.001	0.001	0.001	No Relaxation
Cadmium (mg/l)	0.005	0.005	0.01	0.01	No Relaxation
Arsenic (mg/l)	0.05	0.05	0.05	0.05	No Relaxation
Lead (mg/l)	-	0.05	0.10	0.05	No Relaxation
Chromium (mg/l)	0.1	-	0.05	-	No Relaxation

Table-5 Removal of pollutant from water by functionalized SBA-15

Entry	Functionalized SBA-15	BET (m ² /g)	Pollutant	Maximum adsorption	Reference
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				capacity(q_e)	
1	CuNH ₂ /SBA-15	-	Carbampezine	1.1 μ g/ g	69
2	Fe ₂ O ₃ /SBA-15/CPAA	159	Acid blue 25	909.09 mg/g	70
3	SBA-15	503	Cu (II)	11.39 mg/g	71
4	Zr-SBA-15	688.89	Methylene blue & malachite green	310.88 & 140.61 mg/g	72
5	Ti-SBA-15	1031	Methylene Blue	208.3 mg/g	73
6	γ Fe ₂ O ₃ -SBA-15	983-1049	Arsenic	8.86 mg/g	74
7	MNP-SBA-15	-	Lead	333 mg/g	75
8	ZnO/AlSBA-15	373	Arsenic	123.99	76

6. Conclusion and future perspective

This short review aims to demonstrate the importance of a metal functionalized SBA-15 as efficient catalysts for a wide variety of organic transformations reactions such as cycloaddition, hydrogenolysis, oligomerization, acetylation, reduction, oxidation, amination, crosscoupling, photocatalysis and removal of various contaminants from waste water. With progress in research, there has been a growing trend to continuously move away from homogeneous catalysis to heterogeneous catalysis. In this regard, metal oxide doped SBA-15 continued to shine as a substitute and has been used to carry out a broader array of reactions.

Despite the great success achieved in different functionalized SBA-15 catalysts and significantly accumulative knowledge on its mechanistic aspect by theoretical calculation, several challenges still need to be addressed to explore its full potential. One of the major challenges is the detailed plausible mechanism of formation of transition metal oxide complexes in the catalytic reaction due to its existence in variable oxidation states. With the increased grasp of catalytic pathways, several reactions that are considered challenging will benefit such as the activation of electrophiles for cross-coupling including C–H bonds or O–H derivatives, the formation of C–F, and C–C bonds, and the use of coupling partners like carbon dioxide. Furthermore, coke formation, metal sintering, sulfur poisoning, and deactivation of catalysts have remained

tremendous challenges under reforming conditions. Another considerable challenge is the manageable production of low-cost, core-shell structured catalysts commercially.

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Conflict of Interest

The authors declare no conflict of interest, financial or otherwise.

Reference

- (1) Zhao, D.; Feng, J.; Huo, Q.; Melosh, N.; Fredrickson, G. H.; Chmelka, B. F.; Stucky, G. D. *Science* **1998**, 279 (5350), 548–552. doi: 10.1126/science.279.5350.548
- (2) Zhang, F.; Yan, Y.; Yang, H.; Yan, Y.; Yu, C.; Tu, B.; Zhao, D. *J. Phys. Chem. B* **2005**, 109 (18), 8723–8732. doi: 10.1021/jp044632+
- (3) F das C M, da S.; M J dos S, C.; L K R, da S.; A M, B.; G E, da L., Jr. *SN Appl. Sci.* **2019**, 1 (6). doi: 10.1007/s42452-019-0677-z.
- (4) Singh, B.; Na, J.; Konarova, M.; Wakihara, T.; Yamauchi, Y.; Salomon, C.; Gawande, M. B. *Bull. Chem. Soc. Jpn.* **2020**, 93, 1459–1496. doi: 10.1246/bcsj.20200136.
- (5) Okonye, L. U.; Yao, Y.; Hildebrandt, D.; Meijboom, R. *Sustain. Energy Fuels* **2021**, 5 (1), 79–107. doi: 10.1039/d0se01442g
- (6) Ziarani, G. M.; Roshankar, S.; Mohajer, F.; Badiei, A. *Curr. Org. Chem.* **2021**, 25 (3), 361–387. doi: 10.2174/1385272824999201210194444
- (7) Stevens, W. J. J.; Lebeau, K.; Mertens, M.; Van Tendeloo, G.; Cool, P.; Vansant, E. F. *J. Phys. Chem. B* **2006**, 110 (18), 9183–9187. doi: 10.1021/jp0548725.
- (8) Rahmat. *Am. J. Appl. Sci.* **2010**, 7 (12), 1579–1586. doi:10.3844/ajassp.2010.1579.1586
- (9) Didó, C. A.; Mass, E. B.; Pereira, M. B.; Hinrichs, R.; D'Oca, M. G. M.; Costa, T. M. H.; Russowsky, D.; Benvenuti, E. V. *Colloids Surf. A Physicochem. Eng. Asp.* **2020**, 589, 124455. doi:10.1016/j.colsurfa.2020.124455
- (10) Bhuyan, D.; Saikia, M.; Saikia, L. *Microporous Mesoporous Mater.* **2018**, 256, 39–48.
- (11) Mahato, B. N.; Krithiga, T. *Bull. Chem. React. Eng. Catal.* **2019**, 14 (3), 634. doi:10.9767/bcrec.14.3.4469.634-645
- (12) Li, J.; Bai, X.; Lv, H. *Microporous Mesoporous Mater.* **2019**, 275, 69–75. doi: 10.1016/j.micromeso.2018.08.013sgs

- (13) Kusumawati, E. N.; Sasaki, T. *Green Energy & Environment* **2019**, *4*, 180–189. doi: [10.1016/j.gee.2019.02.003](https://doi.org/10.1016/j.gee.2019.02.003)
- (14) Molaei, S.; Tamoradi, T.; Ghadermazi, M.; Ghorbani-Choghamarani, A. *Polyhedron* **2018**, *156*, 35–47. doi: [10.1016/j.poly.2018.09.014](https://doi.org/10.1016/j.poly.2018.09.014)
- (15) Boosa, V.; Bilakanti, V.; Velisoju, V. K.; Gutta, N.; Inkollu, S.; Akula, V. *Mol. catal.* **2018**, *445*, 43–51. doi: [10.1016/j.mcat.2017.11.007](https://doi.org/10.1016/j.mcat.2017.11.007)
- (16) Bac, S.; Keskin, S.; Avci, A. K. *Sustain. Energy Fuels* **2020**, *4*, 1029–1047. doi: [10.1039/c9se00967a](https://doi.org/10.1039/c9se00967a)
- (17) Zhang, Q.; Sun, M.; Ning, P.; Long, K.; Wang, J.; Tang, T.; Fan, J.; Sun, H.; Yin, L.; Lin, Q. *Appl. Surf. Sci.* **2019**, *469*, 368–377. doi: [10.1016/j.apsusc.2018.10.222](https://doi.org/10.1016/j.apsusc.2018.10.222)
- (18) Zhang, X.; Zhang, L.; Peng, H.; You, X.; Peng, C.; Xu, X.; Liu, W.; Fang, X.; Wang, Z.; Zhang, N.; Wang, X. *Appl. Catal. B* **2018**, *224*, 488–499. doi: [10.1016/j.apcatb.2017.11.001](https://doi.org/10.1016/j.apcatb.2017.11.001)
- (19) Okutan, C.; Arbag, H.; Yasyerli, N.; Yasyerli, S. *Int. J. Hydrogen Energy* **2020**, *45* (27), 13911–13928. doi: [10.1016/j.ijhydene.2020.03.052](https://doi.org/10.1016/j.ijhydene.2020.03.052)
- (20) Chong, C. C.; Teh, L. P.; Setiabudi, H. D. *Mater. Today Energy* **2019**, *12*, 408–417. doi: [10.1016/j.mtener.2019.04.001](https://doi.org/10.1016/j.mtener.2019.04.001)
- (21) Abdullah, N.; Ainirazali, N.; Chong, C. C.; Razak, H. A.; Setiabudi, H. D.; Chin, S. Y.; Jalil, A. A. *Int. J. Hydrogen Energy* **2020**, *45* (36), 18411–18425. doi: [10.1016/j.ijhydene.2019.09.093](https://doi.org/10.1016/j.ijhydene.2019.09.093)
- (22) Desens, W.; Werner, T. *Adv. Synth. Catal.* **2016**, *358* (4), 622–630. doi: [10.1002/adsc.201500941](https://doi.org/10.1002/adsc.201500941)
- (23) Sharma, R. K.; Gaur, R.; Yadav, M.; Goswami, A.; Zbořil, R.; Gawande, M. B. *Sci. Rep.* **2018**, *8* (1), 1901. doi: [10.1038/s41598-018-19551-3](https://doi.org/10.1038/s41598-018-19551-3)
- (24) Monfared, A.; Mohammadi, R.; Hosseini, A.; Sarhandi, S.; Kheirollahi Nezhad, P. D. *RSC Adv.* **2019**, *9* (7), 3884–3899. doi: [10.1039/C8RA10233C](https://doi.org/10.1039/C8RA10233C)
- (25) Jayakumar, S.; Li, H.; Tao, L.; Li, C.; Liu, L.; Chen, J.; Yang, Q. *ACS Sustain. Chem. Eng.* **2018**, *6* (7), 9237–9245. doi: [10.1021/acssuschemeng.8b01548](https://doi.org/10.1021/acssuschemeng.8b01548)
- (26) Li, Y.; Chatterjee, A.; Chen, L. B.; Lam, F. L.-Y.; Hu, X. *Mol. catal.* **2020**, *488* (110869), 110869. doi: [10.1016/j.mcat.2020.110869](https://doi.org/10.1016/j.mcat.2020.110869)
- (27) Akti, F.; Balci, S.; Dogu, T. *Mater. Chem. Phys.* **2019**, *223*, 249–259. doi: [10.1016/j.matchemphys.2018.10.068](https://doi.org/10.1016/j.matchemphys.2018.10.068)
- (28) Awoke, Y.; Chebude, Y.; Márquez-Álvarez, C.; Díaz, I. *Catal. Today* **2020**, *345*, 190–200. doi: [10.1016/j.cattod.2019.09.024](https://doi.org/10.1016/j.cattod.2019.09.024)
- (29) Biswas, R.; Das, S. K.; Bhaduri, S. N.; Bhaumik, A.; Biswas, P. *ACS Sustain. Chem. Eng.* **2020**, *8* (15), 5856–5867. doi: [10.1021/acssuschemeng.9b07409](https://doi.org/10.1021/acssuschemeng.9b07409)
- (30) Tamizhdurai, P.; Sakthinathan, S.; Santhana Krishnan, P.; Ramesh, A.; Mangesh, V. L.; Abilarasu, A.; Narayanan, S.; Shanthi, K.; Chiu, T.-W. *J. Mol. Struct.* **2019**, *1176*, 650–661. doi: [10.1016/j.molstruc.2018.09.007](https://doi.org/10.1016/j.molstruc.2018.09.007)
- (31) Yan, H.; Qin, H.; Feng, X.; Jin, X.; Liang, W.; Sheng, N.; Zhu, C.; Wang, H.; Yin, B.; Liu, Y.; Chen, X.; Yang, C. *J. Catal.* **2019**, *370*, 434–446. doi: [10.1016/j.jcat.2019.01.015](https://doi.org/10.1016/j.jcat.2019.01.015)
- (32) Miao, K.-K.; Luo, X.-L.; Wang, W.; Guo, J.-L.; Guo, S.-F.; Cao, F.-J.; Hu, Y.-Q.; Chang, P.-M.; Feng, G.-D. *Microporous Mesoporous Mater.* **2019**, *289*, 109640. doi: [10.1016/j.micromeso.2019.109640](https://doi.org/10.1016/j.micromeso.2019.109640)
- (33) Jian, J.; Kuang, D.; Wang, X.; Zhou, H.; Gao, H.; Sun, W.; Yuan, Z.; Zeng, J.; You, K.; Luo, H. *Mater. Chem. Phys.* **2020**, *246*, 122814. doi: [10.1016/j.matchemphys.2020.122814](https://doi.org/10.1016/j.matchemphys.2020.122814)
- (34) Deng, T.; Xu, G.; Fu, Y. *Cuihua Xuebao/Chin. J. Catalysis* **2020**, *41* (3), 404–414. doi: [10.1016/S1872-2067\(19\)63505-9](https://doi.org/10.1016/S1872-2067(19)63505-9)
- (35) Zhang, J.; Liu, Y.; Yang, S.; Wei, J.; He, L.; Peng, L.; Tang, X.; Ni, Y. *ACS Sustain. Chem. Eng.* **2020**, *8* (14), 5584–5594. doi: [10.1021/acssuschemeng.9b07512](https://doi.org/10.1021/acssuschemeng.9b07512)

- (36) Fang, C.; Kuboon, S.; Khemthong, P.; Butburee, T.; Chakthranont, P.; Itthibenchapong, V.; Kasamechonchung, P.; Witoon, T.; Faungnawakij, K. *Int. J. Hydrogen Energy* **2020**, *45*, 24054–24065. doi: 10.1016/j.ijhydene.2019.03.272
- (37) Kondeboina, M.; Enumula, S. S.; Gurram, V. R. B.; Chada, R. R.; Burri, D. R.; Kamaraju, S. R. *J. Ind. Eng. Chem.* **2018**, *61*, 227–235. doi: 10.1016/j.jiec.2017.12.020
- (38) Kumaravel, S.; Thiripuranthagan, S.; Erusappan, E.; Durai, M.; Vembuli, T.; Durai, M. *Microporous Mesoporous Mater.* **2020**, *305*, 110298. doi: 10.1016/j.micromeso.2020.110298
- (39) Kot, M.; Kiderys, A.; Janiszewska, E.; Pietrowski, M.; Yang, C.-M.; Zieliński, M. *Catal. Today* **2020**, *356*, 64–72. doi: 10.1016/j.cattod.2019.09.001
- (40) Ungureanu, A.; Chirieac, A.; Ciotonea, C.; Mazilu, I.; Catrinescu, C.; Petit, S.; Marceau, E.; Royer, S.; Dumitriu, E. *Appl. Catal. A Gen.* **2020**, *598*, 117615. doi: 10.1016/j.apcata.2020.117615
- (41) Yu, J.; Cao, J.; Du, L.; Wei, Y.; Wang, T.; Tian, H. *Appl. Catal. A Gen.* **2018**, *555*, 161–170. doi: 10.1016/j.apcata.2018.02.020.
- (42) Melero, J. A.; Moreno, J.; Iglesias, J.; Morales, G.; Fierro, J. L. G.; Sánchez-Vázquez, R.; Cubo, A.; García, B. *Mol. Catal.* **2020**, *484*, 110802. doi: 10.1016/j.mcat.2020.110802.
- (43) Yu, W.; Bhattacharjee, S.; Lu, W.-Y.; Tan, C.-S. *ACS Sustain. Chem. Eng.* **2020**, *8* (10), 4058–4068. doi: 10.1021/acssuschemeng.9b05634
- (44) Pu, Y.; Xuan, K.; Wang, F.; Li, A.; Zhao, N.; Xiao, F. *RSC Adv.* **2018**, *8* (48), 27216–27226. doi: 10.1039/c8ra04028a
- (45) Atakan, A.; Keraudy, J.; Mäkie, P.; Hultberg, C.; Björk, E. M.; Odén, M. *J. Colloid Interface Sci.* **2019**, *546*, 163–173. doi: 10.1016/j.jcis.2019.03.046.
- (46) Chen, K.; Fang, H.; Wu, S.; Liu, X.; Zheng, J.; Zhou, S.; Duan, X.; Zhuang, Y.; Chi Edman Tsang, S.; Yuan, Y. *Appl. Catal. B* **2019**, *251*, 119–129. doi: 10.1016/j.apcatb.2019.03.059.
- (47) Min, L.; Wei, N. A.; Hai-chuan, Y. E.; Hai-hui, H.; Wen-gui, G. *J. Fuel Chem Technol* **2019**, *47* (10), 1214–1225. doi: 10.1016/S1872-5813(19)30048-9
- (48) Jiang, H.; Lin, J.; Wu, X.; Wang, W.; Chen, Y.; Zhang, M. *J. CO₂ util.* **2020**, *36*, 33–39. doi: 10.1016/j.jcou.2019.10.013
- (49) Li, Y.; Zhang, H.; Zhang, L.; Zhang, H. *Int. J. Hydrogen Energy* **2019**, *44* (26), 13354–13363. doi: 10.1016/j.ijhydene.2019.03.276
- (50) Mureddu, M.; Ferrara, F.; Pettinau, A. *Appl. Catal. B* **2019**, *258* (117941), 117941. doi: 10.1016/j.apcatb.2019.117941.
- (51) Babaei, Z.; Najafi Chermahini, A.; Dinari, M. *Chem. Eng. J.* **2018**, *352*, 45–52. doi: 10.1016/j.cej.2018.07.004
- (52) Chen, H.; Ruan, H.; Lu, X.; Fu, J.; Langrish, T.; Lu, X. *Chem. Eng. J.* **2018**, *333*, 434–442. doi: 10.1016/j.cej.2017.09.180.
- (53) Li, S.; Wang, Y.; Gao, L.; Wu, Y.; Yang, X.; Sheng, P.; Xiao, G. *Microporous Mesoporous Mater.* **2018**, *262*, 154–165. doi: 10.1016/j.micromeso.2017.11.027.
- (54) Lima, M. S.; Cruz-Filho, J. F.; Noletto, L. F. G.; Silva, L. J.; Costa, T. M. S.; Luz, G. E., Jr. *J. Environ. Chem. Eng.* **2020**, *8* (5), 104145. doi: 10.1016/j.jece.2020.104145
- (55) Cai, C.; Kang, S.; Xie, X.; Liao, C. *J. Hazard. Mater.* **2020**, *385* (121519), 121519. doi: 10.1016/j.jhazmat.2019.121519
- (56) Bai, L.; Wei, M.; Hong, E.; Shan, D.; Liu, L.; Yang, W.; Tang, X.; Wang, B. *Mater. Chem. Phys.* **2020**, *246* (122825), 122825. doi: 10.1016/j.matchemphys.2020.122825
- (57) Tabaja, N.; Brouri, D.; Casale, S.; Zein, S.; Jaafar, M.; Selmane, M.; Toufaily, J.; Davidson, A.; Hamieh, T. *Appl. Catal. B* **2019**, *253*, 369–378. doi: 10.1016/j.apcatb.2019.04.073
- (58) Jinisha, R.; Gandhimathi, R.; Ramesh, S. T.; Nidheesh, P. V.; Velmathi, S. *Chemosphere* **2018**, *200*, 446–454. doi: 10.1016/j.chemosphere.2018.02.117

- (59) Ghuge, S. P.; Saroha, A. K. *Process Saf. Environ. Prot.* **2018**, *118*, 125–132. doi: 10.1016/j.psep.2018.06.033
- (60) Wei, J. Q.; Chen, X. J.; Wang, P. F.; Han, Y. B.; Xu, J. C.; Hong, B.; Jin, H. X.; Jin, D. F.; Peng, X. L.; Li, J.; Yang, Y. T.; Ge, H. L.; Wang, X. Q. *Chem. Phys.* **2018**, *510*, 47–53. doi: 10.1016/j.chemphys.2018.05.012
- (61) Bai, L.; Wang, S.; Wang, Z.; Hong, E.; Wang, Y.; Xia, C.; Wang, B. *Environ. Pollut.* **2019**, *248*, 516–525. doi: 10.1016/j.envpol.2019.02.052
- (62) Khandekar, D. C.; Bhattacharyya, A. R.; Bandyopadhyaya, R. *J. Environ. Chem. Eng.* **2019**, *7* (5), 103433. doi: 10.1016/j.jece.2019.103433
- (63) Li, G.; Wang, B.; Xu, W. Q.; Han, Y.; Sun, Q. *Dyes Pigm.* **2018**, *155*, 265–275. doi: 10.1016/j.dyepig.2018.03.058
- (64) Calzada, L. A.; Castellanos, R.; García, L. A.; Klimova, T. E. *Microporous Mesoporous Mater.* **2019**, *285*, 247–258. doi: 10.1016/j.micromeso.2019.05.015
- (65) Costa, T. M. S.; Lima, M. S.; Cruz Filho, J. F.; Silva, L. J.; Santos, R. S.; Luz, G. E., Jr. *J. Photochem. Photobiol. A Chem.* **2018**, *364*, 461–471. doi: 10.1016/j.jphotochem.2018.06.039
- (66) Wang, J.; Shao, X.; Liu, J.; Ji, X.; Ma, J.; Tian, G. *Ecotoxicol. Environ. Saf.* **2020**, *190* (110139), 110139. doi: 10.1016/j.ecoenv.2019.110139
- (67) Camposeco, R.; Castillo, S.; Hinojosa-Reyes, M.; Mejía-Centeno, I.; Zanella, R. *J. Photochem. Photobiol. A Chem.* **2018**, *367*, 178–187. doi: 10.1016/j.jphotochem.2018.08.011
- (68) Yamashita, H.; Mori, K.; Kuwahara, Y.; Kamegawa, T.; Wen, M.; Verma, P.; Che, M. *Chem. Soc. Rev.* **2018**, *47* (22), 8072–8096. doi: 10.1039/C8CS00341F
- (69) Ortiz-Martínez, K.; Vargas-Valentín, D. A.; Hernández-Maldonado, A. J. *Ind. Eng. Chem. Res.* **2018**, *57* (18), 6426–6439. doi: 10.1021/acs.iecr.7b05168
- (70) Ghanei, M.; Rashidi, A.; Tayebi, H.-A.; Yazdanshenas, M. E. *J. Chem. Eng. Data* **2018**, *63* (9), 3592–3605. doi: 10.1021/acs.jced.8b00474
- (71) Zhai, Q.-Z. *J. Environ. Chem. Eng.* **2019**, *7* (3), 103069. doi: 10.1016/j.jece.2019.103069
- (72) Ramezani, F.; Zare-Dorabei, R. *Polyhedron* **2019**, *166*, 153–161. doi: 10.1016/j.poly.2019.03.033
- (73) Qiang, T.; Song, Y.; Zhao, J.; Li, J. *J. Alloys Compd.* **2019**, *770*, 792–802. doi: 10.1016/j.jallcom.2018.08.074
- (74) Peng, X.; Zhao, Y.; Yang, T.; Yang, Y.; Jiang, Y.; Ma, Z.; Li, X.; Hou, J.; Xi, B.; Liu, H. *Microporous Mesoporous Mater.* **2018**, *258*, 26–32. doi: 10.1016/j.micromeso.2017.08.050
- (75) Shahabuddin, S.; Tashakori, C.; Kamboh, M. A.; Sotoudehnia Korrani, Z.; Saidur, R.; Rashidi Nodeh, H.; Bidhendi, M. E. *Environ. Sci. (Camb.)* **2018**, *4* (4), 549–558. doi: 10.1039/C7EW00552K
- (76) Mahato, B. N.; Krithiga, T.; Mary Thangam, M. A. *Surf. Interfaces* **2021**, *23*, 100636. doi: 10.1016/j.surf.2020.100636

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