Surface Functionalized Mesoporous Silica Nanoparticles for Enhanced Removal of Heavy Metals: A Review

Aseni Sahasri Pathiraja[1], Imalka Munaweera[1,2,*], Nilwala Kottegoda[1]

[1]Department of Chemistry, Faculty of Applied Sciences, University of Sri Jayewardenepura, Gangodawila, Nugegoda, Sri Lanka
[2]Faculty of Applied Sciences, University of Sri Jayewardenepura, Gangodawila, Nugegoda, Sri Lanka

Date Received: 26/09/2022 Date Accepted: 26-09-2023

Abstract

Human health and environmental sustainability are strongly influenced by the contamination of water resources with hazardous heavy metal ions due to the accumulation in human body via food chains. Thereby, researchers' attention has been paid on effective methods for heavy metal ion scavenging to prevent them releasing to environment. Notably, Mesoporous Silica Nanoparticles (MSNPs) with high surface area, massive surface area to volume ratio, large pore volume and uniform pore distribution play a crucial role in addressing this challenge. Additionally, researchers focus on novel surface functionalization methods of MSNPs with suitable organic and inorganic moieties to amplify the adsorption efficiency of heavy metals. MSNPs possess easily functionalizable surface which facilitates the modifications and enhanced removal of heavy metals. The review article summarizes the different moieties used for functionalization of MSNPs such as amino, thio, carboxyl, phenyl, cyano groups, different types of polymers, inorganic functional groups. Further, a comparison has been made between functional and unmodified MSNPs to elaborate how these modifications have enhanced the removal performance of heavy metals in water. Further, this review provides an overview on different synthesis routes and structure directing agent used in synthesis of MSNPs. Moreover, pH effect on adsorption and reusability of modified NPs, while illustrating the mechanism of adsorption on to modified MSNPs surface has also been elaborated. Maximum adsorption capacity of each functional moiety has been taken into consideration with the aim of supporting future advancements.

Keywords: Adsorption, Mesoporous silica nanoparticles, Heavy metals, Functionalization, Maximum adsorption capacity

Introduction

Pollution of water resources due to the presence of heavy metals occurs mainly owing to global industrialization, fertilizers, pesticides, mining, textile industry, paper manufacturing and electrolysis. Even though some of the heavy metal ions are considered as essential trace elements to human body, consumption of high doses causes damage to the organs. Therefore due to the exceeding the permissive levels given by WHO for heavy metal concentration levels in water, novel methods (Qasem et al., 2021) such as coagulation, ion-exchange (Verbych et al., 2005), chemical precipitation (Chen et al., 2018), membrane processes (Qdais and Moussa, 2004), reverse osmosis and nanofiltration have been introduced. Among these, adsorption is one of the most popular methods.

Adsorption capacity of the adsorbent material depends on several parameters. Particle size, reusability, porosity, capturing selective metal ions from aqueous solutions while maintaining water pH values, low operating cost, eco-friendliness, feasibility of large scale manufacturing, simplicity, structural stability even under adsorption desorption cycles and good interaction between metal ions and the active site of the adsorbents are among them (Da'na, 2017).

Mesoporous silica has been identified as one of the most efficient materials for removal of metal ions in water due to its excellent structural and morphological properties. High surface area, controllable size, large pore volume, uniform pore size which is controlled by surfactants, thermal stability, chemical stability and easy surface functionalization are among the top priorities. For instance, mean pore size of MCM-41, MCM-48, SBA-15, SBA-16 are 3.70nm, 3.48nm, 7.80nm and 5.40nm respectively under particular reaction conditions (Rath et al., 2014). Use of mesoporous silica with different functional moieties is one of the most promising methods for effective capturing of heavy metals. However, there are certain drawbacks in comparison to drawbacks arising from other adsorbents when comparing to MSNPs and this composition is shown in the below table (Table 1).

Table 1: Comparison of MSNPs with other adsorbents for heavy metal ion removal; some drawbacks arising from other adsorbents when comparing to MSNPs.

Adsorbent	Drawback	Reference
Activated Carbon	Non-selective towards target metals Not recommended for removing heavy metals up to permissible ppb levels.	(Gupta et al., 2015)
Multi wall carbon nanotubes	Higher hydrophobicity which leads to rapid aggregation in aqueous solutions owing to van der waals interactions which reduces adsorption potential. Expensive preparation methods.	(Owalude and Tella, 2016), (Qasem et al., 2021)
Chitosan	Lower mechanical strength, less stability and thereby regenerating inefficacy. Powder chitosan lacks porosity, low surface area	(Upadhyay et al., 2021)

**Correspondence: imalka@sjp.ac.lk*

Metal organic framework	Possesses micropores (<2 nm) so, difficult for some metal ions to approach these smaller sites. Less chemical stability.	(Wang et al., 2020)
Magnetic adsorbent	Not sufficiently cyclic stable.	(Qasem et al., 2021)

Even though heavy metal ions are adsorbed to unmodified MS because of surface silanol groups, their removal capacity is not appreciable, therefore there is a need for surface functionalization. However, it is important to note that once the functional groups are incorporated, pore diameter, pore volume and surface area decrease to a certain extent. E.g.: for bare MSNPs, BET surface area is 1048 m^2/g whereas for 3-Aminopropyl functionalized MSNPs, BET surface area is 681 m^2/g (Alswieleh et al., 2021).

Due to the absence of driving forces to absorb heavy metal in unmodified MS, their practical applications are limited. Surface modification techniques have allowed to overcome the drawbacks. However, it should be noted that surface modification reduces the surface-active area of MS while improving the attraction between the heavy metals and surface. The latter forces dominate the efficiency and therefore the removal occurs due to interaction between the surface and heavy metals rather than adsorption.

Furthermore, surface modification with an appropriate functional group improves sensitivity and selectivity due to the synergistic effects arising from the modifier and the MS characteristics.

1 Modifications of Mesoporous Silica Nanoparticles (MSNPs)

1.1 Types of modifications

Researchers have paid attention on modifying MSNPs using several moieties to remove heavy metal ions from water samples. Thus, the below sections are summarize some of the major functionalities used for adsorption of metals such as amino groups, carboxylic, polymers, schiff base while providing qualitative, quantitative ideas on enhanced adsorption performance.

1.1.1 Amino group modification

One of the major functionalization methods is amino modifications and it has gained successful heavy metal ion uptake capacities. Different types of amino modifiers recorded in literature, used to improve functionality are listed as follows. Triethylenetetramine, 3-aminopropyltrimethoxysilane, [3-(2-aminoethylamino)propyl]trimethoxysilane,3-[2-(2-aminoethylamino)ethylamino]propyltrimethoxysilane (Ebrahimi-Gatkash et al., 2017).

3-aminopropyltrimethoxysilane functionalized nano MS was synthesized by Heidari et al. to check the removal capacities of Ni(II), Cd(II) and Pb(II) ions (Heidari et al., 2009). According to the authors, under adsorbent dosage of $5gL^{-1}$, amino functionalized nano MS showed removal percentage values of 92

%, 93 %, 97 % for Ni(II), Cd(II), Pb(II) respectively. (Table 2). Authors further elaborated functionalized materials exhibited higher removal than bare, non-functionalized sorbents while putting forward the idea that nano MS has effectively contributed for scavenging than MS because of the higher surface area of nano MS. Similarly, Lee et al. (Lee et al., 2018) synthesized (3-aminopropyl)trimethoxysilane (APTMS) functionalized MS to enhance chromium removal while changing the amount of amino functionalization on surface from 0.01 M to 0.025 M. Researchers discovered that even though the surface area of synthesized particles decrease with increment of amino functionalization, the effective removal has increased. Another amino functionalization recorded in literature was triethylenetetramine (TETA) functionalized SBA-15 synthesized by Lachowicz et al. (Lachowicz et al., 2019) and used as a sorbent for Cu^{2+} and Zn^{2+} removal (Table 2).

1.1.2 Surface modification using two functional groups

Rather than focusing on one functional group, attention has been paid on modifying a surface with two functional groups simultaneously to gain higher removal properties via synergetic effect. Most frequently amino and carboxylic functionalization is simultaneously used. Zhang et al. (Zhang et al., 2018) developed both amino and carboxyl functionalized spherical mesoporous silica. First, MS was functionalized with polyamino and cyanogen groups followed by hydrolysis of cyanogen to obtain ultimate functionalization. Reported adsorption capacities before and after functionalization were 46.55 mgg^{-1} and 125.57 mgg^{-1} respectively (Table 2). Likewise, Alswieleh et al. synthesized glycine functionalized mesoporous silica nanoparticles which contain amino and carboxylic functionalization (Alswieleh et al., 2021). According to authors, around pH 9, Cu^{2+}, Cd^{2+}, Co^{2+}, Pb^{2+} and Zn^{2+} ions showed more than 85% removal capacity which was achieved through functionalization.

1.1.3 Polymer incorporated to mesoporous silica

Incorporating polymers on to adsorbent surface is also a highlighted section in surface modification of MSNPs. Raei et al. (Raei et al., 2019) reported excellent nickel(II) ion removal by MCM-41 functionalized with 3-mercaptopropyltrimethoxysilane followed by modification with polyaminophenol and observed higher potential of chelating with Ni(II) with maximum adsorption capacity of 16.2 mg/g. Also, Soltani et al. synthesized amino modified MCM-41/poly(vinyl alcohol) nanocomposite, functionalized with amino group initially and then with polyvinyl alcohol (Soltani et al., 2018). Due to abundant surface-active sites, exhibited maximum adsorption capacity for Cd(II) was 46.73 mg/g.

Introducing dendrimers on to MS surface was also studied by Jiang et al. (Jiang et al., 2007). They synthesized highly branched PAMAM (polyamido-amine) dendrimer functionalized SBA-15 and EDTA (ethylenediaminetetraacetic acid) incorporated PAMAM-SBA-15 for heavy metal ions removal. The main concern here was two different modifications showed unrelated binding affinities for target metal ions. However, both modified adsorbents showed higher binding affinity for Pb^{2+}, Zn^{2+} and Cu^{2+}. Yet, PAMAM-SBA-15 showed higher selectivity for Cr^{3+} than Ni^{2+} whereas EDTA-PAMAM-SBA-15 exhibited the vice versa.

1.1.4 Metal immobilized in to mesoporous silica

The theory behind metal immobilization on to MS is introducing a negative center on the surface for increasing the binding affinity of cations and then the increment of heavy metal ion adsorption (Parida and Dash, 2010). Some examples for metal immobilized MS and the acquired removal percentages are as follows. Parida et al. (Parida et al., 2012) embedded different weight percentages of TiO_2; 5, 10, 15, 20

---

*Correspondence: imalka@sjp.ac.lk

and 25% on to MCM-41 to check scavenging capability of toxic Cr(VI) from aqueous medium. 20 wt % TiO_2 loaded MCM-41 achieved 91% of removal percentage and removal capacity recorded for Cr(VI) was 2.32 mmol/g. Their results indicated that, with more than 20 wt % TiO_2, removal of metal ion decreased due to reduction of surface area due to the pore blockage and reduction of pore diameter. Parida et al. prepared trivalent atom Fe^{3+} incorporated MCM-41 for Cu^{2+} ion removal where 81% removal percentage was obtained with 59.6 ppm Cu^{2+} ion concentration. (Parida and Dash, 2010).

1.1.5 Other types of functional groups

Other than above mentioned modifiers, various different kinds of modifiers have been used to maximize adsorption efficiency. Some of them are melamine – formaldehyde – thiourea resin, schiff base, mecaptopropylsilyl, sodiumdodecylsulphate, tetrakis(4-carboxyphenyl) porphyrin and diethylphosphatoethyl group.

Yu et al. (Yu et al., 2021) synthesized SBA-15 incorporated with melamine – formaldehyde – thiourea resin via co-condensation where “chelation resin” functional moiety is a novel insight in ‘heavy metal removal’ extreme. Zhang et al. (Zhang et al., 2020) synthesized pyridyl schiff base functionalized MS for Cu(II) and Pb(II) adsorption from aqueous solution (Table 2). Two schiff bases they used were, N-propyl-2-pyridylimine (PA) and ethylenediaminepropyl-2-pyridylimine (NPA). However, NPA functionalized MS has shown higher maximum adsorption capacity than PA functionalized MS due to the presence of higher amount of nitrogen atoms in NPA. Wang et al. (Wang et al., 2018) functionalized MSNPs with cyano groups using 2-cyanoethyltriethoxysilane (CTES) for Cd^{2+} and Ni^{2+} removal. Similarly, MS was functionalized with CTES for Cr(III) removal by Gervas et al. (Gervas et al., 2016). Wongsakulphasatch et al. synthesized MCM-41 functionalized with Sodiumdodecylsulphate (SDS) (Wongsakulphasatch et al., 2014) and checked removal efficiency for Cu^{2+} and Zn^{2+}. Further Jeong et al. (Jeong et al., 2011) introduced novel tetrakis(4-carboxyphenyl) porphyrin incorporated SBA-15 via the post-grafting method of scavenging Cu(II) ions from aqueous solutions. MS functionalized with hydroxyphosphatoethyl (POH) group was introduced by Gunathilake et al. (Gunathilake et al., 2015) for the uptake of Pb^{2+} ions, where a higher affinity has been resulted towards the target metal ions.

Apart from the above mentioned conventional organic functional moieties, inorganic groups such as ferrocene incorporation on to MSPNs has taken place. Yang et al. (Yang et al., 2019) designed ferrocene incorporated MSNPs. Specific advantages of ferrocene incorporating on to MS are non-toxicity, stability and facilitating heavy metal ion adsorption via non-covalent interactions (Yang and Liu, 2018).

Figueira et al. developed thiol group incorporated periodic mesoporous organosilica which is a novel insight in the field (Figueira et al., 2017). They paid attention on reducing the thiol dosage because high density of thiol causes toxic effects (Munday, 1989). Authors stated that, this was reported as the lowest thiol functionalization ever used.

Table 2: Maximum adsorption capacities exhibited by different functional groups incorporated on to MS

Adsorbent	Experimental Conditions	Best Isotherm	Maximum Adsorption Capacity (mg/g)	Reference

NH_2-MCM - 41	Adsorbent dosage – 5 mg/L pH – 5	Langmuir	12.36 (Ni^{2+}) 18.25 (Cd^{2+}) 57.74 (Pb^{2+})	(Heidari et al., 2009)
TETA-SBA-15	Adsorbent dosage – 3 mg in 10 ml of metal ion solution pH – 4 Temperature – 298 K	Langmuir	23.9 (Cu^{2+}) 13.6 (Zn^{2+})	(Lachowicz et al., 2019)
MSS-NH_2-COOH	Adsorbent dosage – 200 mg/L pH – 5 Temperature – 25°C	Freundlich	122 (Ni^{2+}) 12.11 (Zn^{2+}) 98.18 (Cr^{6+})	(Zhang et al., 2018)
SBA-PA SBA-NPA	Adsorbent dosage – 40 mg pH – 5	Langmuir	35.87 (Cu^{2+}) 82.05 (Pb^{2+}) 48.26 (Cu^{2+}) 10.62 (Pb^{2+})	(Zhang et al., 2020)
N-[3-(trimethoxysilyl) propyl] diethylenetriamine functionalized MS	Adsorbent dosage – 50 mg in 20 cm^3 of aqueous solution Temperature – 298 K	Langmuir	2.2 mmol/g (Cu^{2+}) 2.8 mmol/g (Ni^{2+})	(Dey et al., 2008)
Amine modified MCM-41/poly (vinyl alcohol) nanocomposite	Adsorbent dosage – 0.01 mg Temperature – 298 K 4hrs shaking time	Langmuir	46.73 mg/g - Cd(II)	(Soltani et al., 2018)
Aminopropyl functionalized MS	Adsorbent dosage – 50 mg Temperature – 20°C pH – 5 Equilibrium time – 20 min	Langmuir	111.1 mg/g – Cr(VI)	(Idris et al., 2012)

.

1.2 Adsorbent morphology

Synthesizing MSNPs with different morphologies such as fibrous KCC-1, cubic ordered KIT-6, wrinkled shape nanoparticles has become a leading development in current field. Yan et al. (Yan et al., 2019) developed thiol functionalized MSNPs with 3 distinct morphologies namely; wrinkled nanospheres, MSNPs with concavities and sunken nanovesicles by altering the added amount of $NH_3.H_2O$. Among above three, functionalized wrinkled mesoporous silica has gained highest surface area, pore volume and average pore size. Values reported were 499.5 m^2/g, 1.2 cm^3/g and 16.2 nm respectively. As a result, the adsorbent with wrinkled morphology has exhibited highest adsorption capacity of 87.3 mg/g for Hg^{2+} ions

---

**Correspondence: imalka@sjp.ac.lk*

removal when comparing to other two morphologies. Novel fibrous silica nanosphere KCC-1 has gained much attention currently due to its fibrous morphology (Soltani et al., 2020) and the excessive amount of easily accessible silanol moieties on the surface of KCC-1 has widely increased the functionalization potential (Soltani et al., 2019). Similarly, Marjani et al. (Marjani and Mohammadi, 2021) synthesized KCC-1 modified with tetra-sulfide and reported maximum adsorption capacity value of 129.73 mg/g.

Rabie et al. (Rabie et al., 2019) prepared cubic ordered KIT-6 silica adsorbent modified with ethylenediamine and compared removal percentages values of functionalized and non-functionalized materials. They found that reported values for removal rate and maximum adsorption capacity were 95.6% and 50 mg/g respectively for functionalized particles whereas adsorption rate of non-functionalized KIT-6 was much lower than those values with 82.5% removal rate and $38mgg^{-1}$ maximum adsorption capacity. Ge et al. (Ge et al., 2018) studied the impact of framework structure, surface of adsorbent pore size and channel shape of nitro and-amino functionalized mesoporous silica series SBA-15, KIT-6 and SBA-12. According to the authors, amount of amine functionality on the surface was in the ascending order of non-porous SiO_2, KIT-6, SBA-15 and SBA-12. But the reported maximum adsorption capacity of Cu^{2+} was in the ascending order of SBA-15 (27.4 mg/g), SBA-12 (46.6 mg/g) and KIT-6 (47.8 mg/g). Authors suggest that the reason for this may be the coordination of Cu^{2+} and amine groups in different frameworks rather than the amine functional groups.

Bagheri et al. (Bagheri et al., 2019) selected three thiol-functionalized mesoporous silica morphologies including SBA-15-SH, MCM-41-SH with hexagonal framework and KIT-6-SH with cubic geometry, for detection of cadmium ions removing efficiency. According to Langmuir adsorption isotherm data, structurally similar SBA-15 and MCM-41 manifested similar adsorption behavior while on the contrary, KIT-6 showed different adsorption behavior exhibiting the highest maximum adsorption capacity of 85 mg/g. Even though, all 3 morphologies possess interconnected pore system allowing fast diffusion, kinetics of KIT-6-SH was little lower than other two. Authors have suggested a reason that pore connecting channels are not in the same size of the pores, thereby slightly blocking the diffusion in KIT-6-SH.

2 Routes of introducing functionality

2.1 Synthesis methods

There are several ways of incorporating functional moieties on to silica surface. Among them, post grafting (where the attachment of functional moieties on to silica surface takes place) (Figure 1) and co-condensation (where the functional moieties have been inserted to the silica matrix) are highlighted.

Putz, A.M. et al. (Putz et al., 2021) have done a comparison between these two methods for the Cr(VI) removal using mono amino functionalized MS; MCM-41. According them, after performing the adsorption study at pH 3.5 for 2h at 298 K temperature, maximum adsorption capacity reported for co-condensed material was 85.5 mg/g and 9.4 mg/g for grafted material, demonstrating that co-condensation has gained 10 times more efficacy than post grafting. On the other hand, Aguado et al. (Aguado et al., 2009) provided an idea which contrasts with above. They conducted an experiment in a similar manner and proved that material synthesized using post grafted technique has effectively contributed to heavy metal ion removal. They stated that, although there was high nitrogen content in co-condensed amino SBA-15, any detectable removal capacity was not observable as amino groups on silica surface were not accessible to heavy metals in a sufficient manner.

Yokoi et al. (Yokoi et al., 2004) stated a relationship between co-condensation, post – grafting and number of amino functional groups on the surface. Cations adsorption on to amino functionalized MCM-41 via co-condensation increased with increment of amino groups; in the order of mono-, di-, tri-. But this order has not been reported in post – grafting. In post – grafting method, although adsorption capacity of mono and diamino increase with density of surface functional groups, adsorption capacity of NNN–silane anchored MS decreased when surface density of amino groups increasing. Therefore, authors suggest that positions of amino groups on the surface depends on synthesis method.

Additionally, Huang et al. (Huang et al., 2012) synthesized functional SBA-15 functionalized with amino groups and EDTA using a two-step post grafting technique, where the functional moiety was introduced to silica wall in a step wise manner; anchoring 3-aminopropyltrimethoxysilane followed by EDTA.

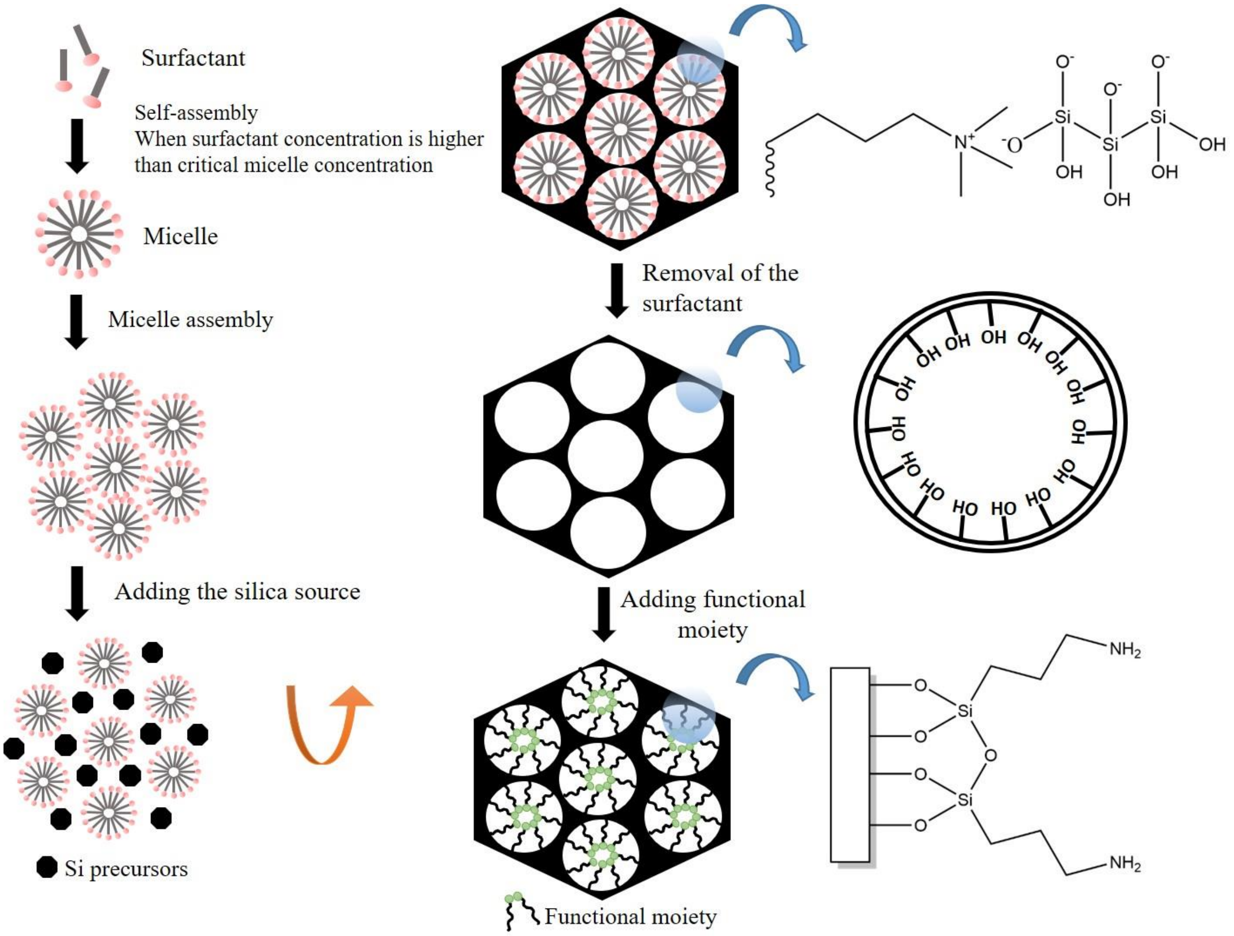

Figure 1: A diagrammatic representation of post – grafting method in the synthesis of Mesoporous Silica Nanoparticles.

**Correspondence: imalka@sjp.ac.lk*

2.2 Different structure directing agents

Synthesizing MSNPs is accompanied by template-based method in which micelles are formed using surfactant. In co-structure directing agent route, an interaction is formed between head group of surfactant and co-structure directing agent (Huang and Che, 2015). Yokoi et al. (Yokoi et al., 2006) put forward an explanation of using anionic surfactant; Lauric Acid Sodium salt (LAS) to achieve mesoporous nature. Anionic head group of lauric acid interact with cationic head group of amine silane coupling agent "3-aminopropyltriethoxysilane" (APS) via electrostatic interactions and form silica – micelle template. According to researchers, amount of surface amino groups from APS detected by CHN elemental analysis were 2.36 mmolg^{-1} and that amount is considerably higher than surface amino propyl groups in MCM-41 synthesized using cationic surfactant route. (Figure 2) Thus, they stated the adsorption of Co^{2+} ions in to MS templated via anionic surfactant has increased adsorption capacity with respect to cationic surfactant.

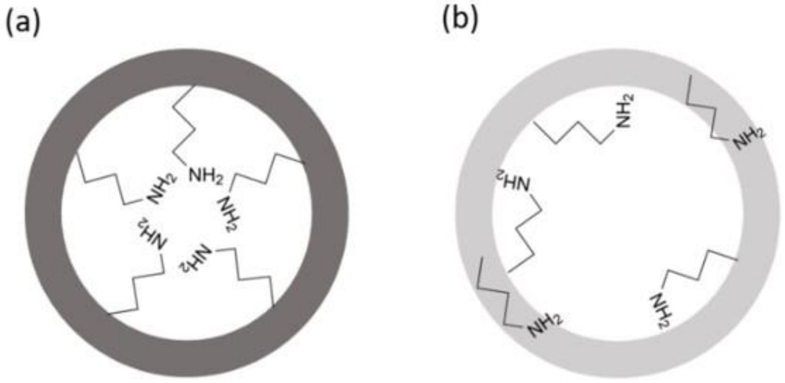

Figure 2: Location of the amino groups on surface of MCM-41 when synthesized using (a) anionic surfactant route (b) cationic surfactant route.

Showkat et al. (Showkat et al., 2007) prepared co-condensed N-[3-(trimethoxysilyl)-propyl] aniline modified mesoporous silica using three surfactants; dodecyl, cetyl, eicosane trimethyl ammonium bromide. Pore diameter, pore volume have been changed depending on the structure directing agent and authors mentioned that these factors have made an impact on the removal percentage of Cr(VI), As(V), Pb(II) and Hg(II) ions. Due to the higher N amount (2.1mmol/g), MCM-41 prepared with eicosane trimethyl ammonium bromide than other two, it showed higher maximum adsorption capacity (0.85 mmol/g) for As(V), 0.78 mmol/g for Pb(II) and 0.92 mmol/g for Hg(II).

However, Jia et al. (Jia et al., 2019) stated that the traditional surfactant causes some issues such as fairly lower amount of amino groups and aggregating nanoparticles. Therefore, a novel anionic gemini surfactant was used to prepare amino modified MSNPs to capture Pb^{2+} ions from polluted wastewater. Unlike conventional surfactant, this gemini surfactant with two non-polar hydrophobic tails and polar head groups tend to gain high amino loading which is evenly distributed on the surface and specifically a lower critical micelle concentration is needed (Li et al., 2013). Here, researchers have used di-laurel acyl ethylenediamine diacetate sodium as anionic gemini surfactant and 3-aminopropyltrimethoxysilane as co-structure directing agent. As declared by authors, this excellent adsorption capacity was gained definitely due to high N content in adsorbent which is acquired due to novel surfactant.

On the other hand, Gao et al. (Gao et al., 2017) stated that there are some disadvantages of using surfactant as structure directing agent such as toxicity of surfactant, removing surfactant via calcination leads to losing silanol functionalities and the high cost effect. Hence, they synthesized novel, excellent sorbent with interconnected pores using non-surfactant template; tannic acid. Dopamine functionalized tannic acid templated MSNPs were used for Cu^{2+} ion removal. According to authors, when increasing Cu^{2+} concentration from 20 to 300 ppm at 298 K and at pH 5.5 with 1.0 g/L Dop-TMSN dosage, the reported adsorption capacity was 58.7 mg/g.

2.3 Template removal procedure

Calcination, extraction using a solvent and micro-wave assisted methods are most commonly used template removal methods in the synthesis route of MSNPs. Template removing using microwave digestion has gained researchers' attention lately. It is assumed that higher pore size with mesopore tunnels is because of combining two or three SBA - 15 pores after the teardown of pore walls during the applied microwave power (Gu et al., 2008). Idris et al. (Idris et al., 2011) performed template removal via microwave digestion using nitric acid and hydrogen peroxide and compared it with conventional calcination template removal method. According to analyzed data, even though BET surface area has slightly reduced when surfactant was removed by microwave digestion than calcination, average pore size of the microwave digested material increased significantly up to 6.74 nm which is a quite uncommon value for average pore size of MSNPs.

Gascón et al. (Gascóna et al., 2019) focused mainly on the efficiency of template removal method; either calcination or extraction. They synthesized SBA – 15 mesoporous silica and grafted mono- and di- amino groups containing functional moieties which act as adsorbent for Pb(II) and Cd(II) uptake. In the samples where surfactant was removed using extraction, a higher maximum adsorption capacity for Pb(II) was reported for triamine functionalized one rather than diamine due to higher amount of N content. But this concept has changed entirely, when calcination was used for template removal. SBA-15-C-NN-30% has shown an improvement in adsorption capacity compared to SBA-15-C-NNN-30%. Authors have emphasized that this is due to the less probability of having available silanol groups in SBA-15 material after calcination and therefore less incorporation of amino groups during post-grafting.

3 Factors affecting adsorption

3.1 Selectivity of a functional group

Selectivity of a functional moiety towards a particular target ion depends on the diameter of the cavity formed by functional group, ionic radius of the target atom and the hard-soft acid base theory.

Liu et al. (Liu et al., 2000) synthesized thiol and amino functionalized SBA-15 mesoporous silica and they found that thiol modified adsorbent showed higher binding ability for Hg^{2+} ions whereas the corresponding amino analogue showed high complexation affinity for Cu^{2+}, Zn^{2+}, Cr^{3+} and Ni^{2+}. Explanation has been made using hard soft acid base theory. Authors suggested that ligands with softer donor atoms form stable complexes with softer transition metal ions, thiol group; softer donor shows higher affinity with softer metal ions; Hg^{2+}. On the other hand, since the ligands with harder donor atoms

---

**Correspondence: imalka@sjp.ac.lk*

form stable complexes with harder metal ions, harder donors such as amino groups bind with harder metal ions such as Cu^{2+}, Zn^{2+}, Cr^{3+} and Ni^{2+}.

Lei et al. (Lei et al., 2015) introduced amino-modified Mn loaded SBA-15 and selectively trapped Cu^{2+} ions on to binding sites where Mn oxide was successfully loaded. Authors mentioned that such hybrid adsorbent with the combination of metal-organic-inorganic MS was not reported yet for selective removal of Cu^{2+}. They found out that NH_2-Mn-SBA-15 has heavy metal uptake capacity of 35.39 mg/g even in the presence of Pb^{2+}, Zn^{2+}, Cd^{2+}. Further the adsorption capacity (for a solution merely with Cu^{2+} ions) was reported as 40.67 mg/g which illustrates that there is only a slight difference between adsorption capacities. Similarly, to selectively remove Ni^{2+} ions from aqueous waste, He et al. (He et al., 2018) developed Ni^{2+} imprinted iminodiacetic acid (IDA) functionalized SBA-15 and ethanediamine functionalized MCM-41. Both adsorbed Ni^{2+} at two different pH conditions. They reported that IDA functionalized SBA-15 fitted for acidic water treatment whereas ethanediamine functionalized MCM-41 was suitable for alkaline wastage because it reached up to 20.8 mg/g Ni^{2+} removal capacity at pH 6. To investigate the exact trapping target metal ion by adsorbent, the experiment was performed by them in the presence of other competitive metal ions with same ionic radius as Ni^{2+}. Eventually the researchers concluded that only Ni^{2+} traps inside the functional cavity because of its size.

Sarafraz et al. (Sarafraz et al., 2017) synthesized MS modified with phosphonic groups for the selective removal of toxic U(VI) ions from aqueous effluents obtaining a maximum adsorption capacity of 206 mg/g and 79.82 % recovery percentage for U(VI) even in the presence of other metals.

Tapaswi et al. (Tapaswi et al., 2014) introduced novel 1,4,7-triazacyclononane (TACN) functionalized MS and discussed its specific selectivity towards Cu^{2+} in the presence of other metals; Cr^{3+}, Ni^{2+}, Co^{2+} and Li^{+}. As stated by authors, selectivity has been aroused due to the small cavity in TACN functional moiety that fit to Cu^{2+} ions specifically.

MCM – 41 functionalized with Sodiumdodecylsulphate exhibited higher removal for Cu^{2+} than Zn^{+2} and this incident was explained by authors as follows. Because of the higher charge to diameter ratio of Cu^{2+}, it has higher electronegativity than Zn^{2+} and this has led to higher affinity of Cu^{2+} with functional groups (Wongsakulphasatch et al., 2014).

3.2 Effect of solution pH on adsorption

Mohammadnezhad et al. (Mohammadnezhad et al., 2019) stated that adsorption capacity of Cu^{2+} on to amino modified MCM-41 functionalized with poly(methyl methacrylate) differs with pH. When conditions were set to 10 mg/L concentration of Cu^{2+}, 0.5 g/L nanocomposite, 180 rpm shaking rate at 298 K for 240 minutes, the removal capacity increased from pH 2 to 4. They also claimed that the reason for decline of adsorption below 2-4 pH range is due to the competition between proton and Cu^{2+} ions on to amine groups.

Jang et al. (Jang et al., 2020) investigated that amino functionalized MS increased adsorption capacity of Cr(VI) from 11.8 mg/g to 40.8 mg/g when pH decreased from 7 to 2 and they put forward a wide illustration on how pH affects adsorption. They showed a relationship between adsorbent's surface charge and the form of which Cr(VI) present in a solution at a particular pH. Cr(VI) presents as H_2CrO_4 at strong acidic pH values (<2) whereas between pH 2 and 6, Cr(VI) presents as $HCrO_4^-$ and $Cr_2O_7^{2-}$. On the other hand, since the pH_{pzc} value on adsorbent surface is pH 8.4, below that pH value, NH_2 exists as

NH_3^+ and silanol group also gains a positive charge. Therefore, as a consequence, the electrostatic interactions tend to form between anionic Cr(VI) species and cationic sorbent within this pH range.

Wu et al. (Wu et al., 2015) designed a manganese dioxide loaded MS for Cr(VI) and As(III) ion removal. As stated by authors, maximum adsorption was reported for As(III) at pH 4 because As(III) exists as $H_3As_3^0$; neutral species within 2 to 4 pH range and that leads to maintain van der waals interactions within adsorbent and adsorbate. Further in the range of pH 4 - 6.9, $H_2AsO_3^-$ was the dominant species and reduction of adsorption capacity has been observed due to repulsion between negatively charged sorbent and $H_2AsO_3^-$. Regarding this case, another interesting factor put forward by authors was MnO_2 acting like an oxidant powder and plays a role in oxidizing $H_3As_3^0$ and $H_2AsO_3^-$ to As(V) oxidation state which can readily be precipitated.

3.3 Effect of counter anion on adsorption process

Anions present in solution also play a main role in adsorption in different manners. Anionic effect was tested by Lam et al. (Lam et al., 2008) for Cu^{2+} adsorption on to amino modified MCM-41 from $Cu(NO_3)_2$ and $CuSO_4$ solutions and found out that adsorption was higher in SO_4^{2-} anion. Even though 70 % of binding sites were readily approachable for Cu^{2+}, the rest is only accessible when SO_4^{2-} anions are there. According to experimental data presented by researchers, 2.3 mmol/g amino loading achieved 0.76 mmol/g Cu^{2+} from $Cu(NO_3)_2$ and 1.33 mmol/g Cu^{2+} from $CuSO_4$ which is 50% more. Authors presented reasons for this as follows. SO_4^{2-} ions interact with dissolved Cu^{2+} ions to form $[Cu\ SO_4]^\circ$ species (Figure 3) and promote adsorption at the later part when it was reaching to saturation. Also, they coadsorb with Cu^{2+} ions in order to form stabilized coordination complexes with individual aminopropyl sites and also in unfavorable and isolated aminopropyl entities. And finally, SO_4^{2-} reacts with silanol groups to release aminopropyl for increased Cu^{2+} adsorption. Also, they reported that SO_4^{2-} promotes 3-aminopropyl sites adsorbing two Cu^{2+}.

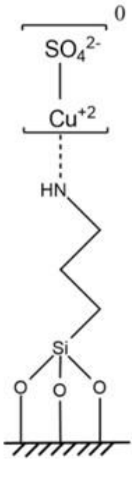

Figure 3. Chemical illustration of the $[CuSO_4]^0$ species adsorbed on to amino functionalized MCM – 41.

3-mercaptopropyltrimethoxysilane modified MCM-41 was utilized for Cu(II) adsorption by Wu et al. (Wu et al., 2010) and they reported how the anions influenced the adsorption in the order of $NO_3^- <$

**Correspondence: imalka@sjp.ac.lk*

OAc^- < SO_4^{2-} < CO_3^{2-} < Cit^- < Cl^-. This order has strictly depended on coordination capability of each anion. Such that Cl^- ions readily interact with Cu^{2+} and form stable $CuCl_4^-$ complexes unlike other anions and interfere the adsorption on to active sites on surface. Thus, when there are NO_3^- ions, reported removal rate was 84.3 % whereas, it was 36.4 % in the presence of Cl^- anions. The same order for the influence of anion on adsorption has been observed by Xue et al. (Xue and Li, 2008) for Cu(II) adsorption. NO_3^- < OAc^- < SO_4^{2-} < Cit^- < Cl^- on to 3-mercaptopropyltrimethoxysilane modified SBA-16. Researchers claimed that in the presence of NO_3^- ions 25.34 mg/g adsorption capacity was observable while on the contrary, the value reported in the presence of Cl^- ions was 17.85 mg/g. They also have stated the same reason as Wu et al. did.

3.4 Reusability of modified MSNPs

Furthermore, there is an important factor when developing water treatment technology. The reusability of the adsorbent guarantees the user-friendliness. Jadhav et al. (Jadhav et al., 2021) synthesized 3-aminopropyltriethoxysilane functionalized MSNPs and illustrated the reusability effects of adsorbent using the explanation using the pH values. They recorded maximum adsorption capacity value for Cr(VI) of 50 mg/g around pH 1. This MSNPs showed 87% and 96% removal capacity respectively at pH 2 and 1 which means a considerably higher adsorption efficiency has required at acidic low pH values. This concept has been used to develop the recycling of nanoparticles. They have selectively captured Cr(VI) at acidic pH and recovery was achieved by increasing the pH to basic value because the complex between adsorbent and adsorbate is broken down at higher pH values. Likewise, they have reused AMSNPs up to 5 cycles retaining 81% removal percentage of Cr(VI).

3.5 Adsorption mechanism associated with modifications

The applicable mechanism behind the binding of heavy metal ions to functional group is described in many extremes with respect to hard soft acid base theory and chelation mechanism. Han et al. (Han et al., 2021) showed how pH affects the adsorption behavior of Mn^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+} and Pb^{2+} on to amine modified MCM-48. According to them, since the metal ions exist as M^{+2}, $M(OH)^+$, $M(OH)_2$ in alkaline and neutral pH, adsorption mechanism could be explained by chelating effect, H bonding and electrostatic interactions (Figure 4).

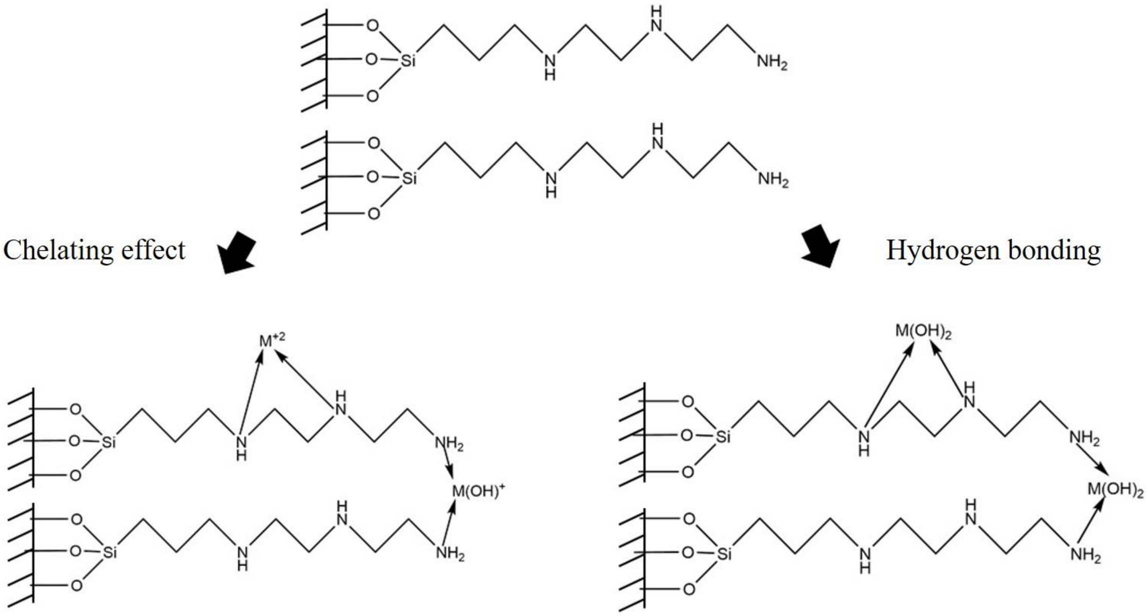

Figure 4: Adsorption mechanism of divalent metal ions on to amino modified MCM - 48

Yantasee et al. (Yantasee et al., 2003) tested the feasibility of utilizing acid forms of carbamoylphosphine ligand on to MS in order to isolate heavy metal ions from aqueous waste. The two types of analogues they have chosen were acetamide phosphonic acid and propionamide phosphonic acid (PPH). So that M^{2+} divalent metal ions have the capability of chelating with diprotic functional group and amide ligand. They stated that sorption of metal ions on to acetamide phosphonic acid (APA) has higher potential than other counter-part, due to the six membered chelate ring in APA analogue favors trapping small heavy metal ions whereas seven membered chelating ring in PPH is much less likely to capture metal ions. However, authors have declared that further studies are required to evaluate precisely the mechanism of heavy metal ions binding to carbamoylphosphonic acid. In triethylenetetramine (TETA) functionalized SBA-15, stable complexes were formed by TETA with Cu^{2+} and Zn^{2+} because of the four chelating amino groups; two primary and two secondary (Lachowicz et al., 2019).

Regarding the mechanism of adsorption, Gascóna et al. (Gascóna et al., 2019) proposed a reason for the two different affinities of Pb^{2+} and Cd^{2+} towards amino groups incorperated on to MS. In accordance with that, since Cd^{2+} is a soft acid and Pb^{2+} is a border line acid, while aliphatic nitrogens are considered as harder base, Pb^{2+} shows higher affinity towards amine modified silica adsorbent. Also, they pointed out that metal ions tend to form tetra-linked complexes involving four Nitrogen atoms and also there is a sort of involvement of surface silanol groups for complex formation. Chelating mechanism between phosphonic group and Pb^{2+} has been put forward by Gunathilake et al. (Gunathilake et al., 2015). As they mentioned, two electrones at oxygen are donated to Pb^{2+} which lacks electrones to form a strong ionic interaction with a huge difference in electronegativity according to the pearson hard soft acid base theory (Figure 5).

---

*Correspondence: imalka@sjp.ac.lk

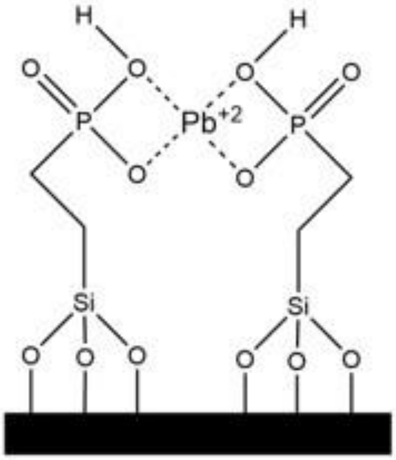

Figure 5: Hypothetical coordination structures for lead ion adsorption on to phosphonic groups

4 Future potentials of modified MSNPs

MSNPs have been greatly exploited for heavy metal ion removal owing to its distinct properties. Several functionalization; organic and inorganic are incorporated on to MS with the aim of utilizing this nanomaterial as an efficient adsorbent.

Nevertheless, still there exists some bottlenecks that ought to be overcome. First and foremost, attention should be paid on the toxicity of functional moiety that is used for modification as it is directly exposed to water. If that particular group leads to environmental pollution and it causes hazardous effects to aqueous lives, the total damage induced by functional group is higher than the heavy metal ion impact. So, care should be taken to select the correct modification. Thereby the biocompatibility of nanomaterial with environment needs to be further investigated. On the other hand, with time, aggregation of nanomaterials takes place which leads to reduction of removal efficacy. And also, removal of nanoparticles from solutions after the treatment is also difficult since nanoparticles tend to disperse in solution due to its nanoscale size. The removing efficacy associated with MSNPs decreases after utilizing for few cycles due to the loss of functional moiety. Precautions can be taken to minimize this loss and to increase the reusable cycles.

Additionally, developing MSNPs as conventional material for heavy metal ion remediation is still on discussion. Efforts must be taken to develop this nanomaterial as a low-cost market available material.

5 Conclusion

During the past few decades, MSNPs are used as a promising nanoadsorbent for the heavy metal ion remediation due to its unique properties such as higher surface area, uniform pore distribution, open porous nature to facilitate the access of functional groups. Further, functional moieties on the surface act as active sites to enhance heavy metal ion binding and for selective adsorption of target metal ions. MSNPs functionalized with amino, thio, carboxyl, phenyl, cyano groups, different types of polymers and inorganic functional groups exhibit excellent removal capacities for heavy metal ions such as Ni^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+} and Co^{2+}. However, the major challenges that should be overcome regarding to this field are 1) regeneration of NPs, 2) large scale applications, 3) environmental hazards caused by organic counter parts, 4) selective adsorption of targeted metal ions, 5) avoiding the dispersion of NPs in aqueous solutions.

Methods are introduced to recycle the used adsorbents with the aim of reducing secondary pollution. Using appropriate reagents, the number of generation cycles can be expanded up to several times. Since some organic moieties used for functionalization is hazardous for aquatic life and human body, number of functional moieties generated should be reduced by increasing the number of regeneration cycles. Further, there is a limitation of commercially available agents and thus, again it says regeneration of used MSNPs is a significant factor. On the other hand, targeting the particular metal ion that is required to be removed is also a challenging task.

Even though, many researchers have introduced novel functionalized MSNPs for heavy metal ion removal, most of them can only be utilized in laboratory scale applications. Efforts must be taken to encourage developing highly sophisticated methods to remove heavy metal ions in the industrial scale in real water samples.

Taking all in all, if all the challenges are met, developing a cost-effective, non-toxic, stable, eco-friendly, commercial adsorbent will happen in near future.

6 Abbreviations

MSNPs – Mesoporous Silica Nanoparticles

MS – Mesoporous Silica

MCM-41 – Mobil Composition of Matter No. 41

MCM-48 – Mobil Composition of Matter No. 48

SBA-15 – Santa Barbara Amorphous – 15

SBA-16 – Santa Barbara Amorphous – 16

References

Aguado, J., Arsuaga, J. M., Arencibia, A., Lindo, M. & Gascón, V., 2009. Aqueous heavy metals removal by adsorption on amine-functionalized mesoporous silica. Journal of hazardous materials. 163**,** 213-221.

Alswieleh, A. M., Albahar, H. Y., Alfawaz, A. M., Alsilme, A. S., Beagan, A. M., Alsalme, A. M., Almeataq, M. S., Alshahrani, A. & Alotaibi, K. M., 2021. Evaluation of the adsorption efficiency of glycine-, iminodiacetic acid-, and amino propyl-functionalized silica nanoparticles for the removal of potentially toxic elements from contaminated water solution. Journal of Nanomaterials. 2021.

Bagheri, S., Amini, M. M., Behbahani, M. & Rabiee, G., 2019. Low cost thiol-functionalized mesoporous silica, KIT-6-SH, as a useful adsorbent for cadmium ions removal: a study on the adsorption isotherms and kinetics of KIT-6-SH. Microchemical Journal. 145**,** 460-469.

Chen, Q., Yao, Y., Li, X., Lu, J., Zhou, J. & Huang, Z., 2018. Comparison of heavy metal removals from aqueous solutions by chemical precipitation and characteristics of precipitates. Journal of water process engineering. 26**,** 289-300.

Da'na, E., 2017. Adsorption of heavy metals on functionalized-mesoporous silica: A review. Microporous and Mesoporous Materials. 247**,** 145-157.

**Correspondence: imalka@sjp.ac.lk*

Dey, R. K., Oliveira, F. J. & Airoldi, C., 2008. Mesoporous silica functionalized with diethylenetriamine moieties for metal removal and thermodynamics of cation–basic center interactions. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 324**,** 41-46.

Ebrahimi-Gatkash, M., Younesi, H., Shahbazi, A. & Heidari, A., 2017. Amino-functionalized mesoporous MCM-41 silica as an efficient adsorbent for water treatment: batch and fixed-bed column adsorption of the nitrate anion. Applied Water Science. 7**,** 1887-1901.

Figueira, P., Lourenço, M., Pereira, E., Gomes, J., Ferreira, P. & Lopes, C., 2017. Periodic mesoporous organosilica with low thiol density–a safer material to trap Hg (II) from water. Journal of Environmental Chemical Engineering. 5**,** 5043-5053.

Gao, J., Lei, H., Han, Z., Shi, Q., Chen, Y. & Jiang, Y., 2017. Dopamine functionalized tannic-acid-templated mesoporous silica nanoparticles as a new sorbent for the efficient removal of Cu2+ from aqueous solution. Scientific Reports. 7**,** 1-11.

Gascóna, V., Arencibiab, A. & Arsuagab, J. M., 2019. Efficient amine-SBA-15-type adsorbents for treatment of water containing trace levels of Pb (II) and Cd (II). Desalination and Water Treatment. 146**,** 210-226.

Ge, S., Geng, W., He, X., Zhao, J., Zhou, B., Duan, L., Wu, Y. & Zhang, Q., 2018. Effect of framework structure, pore size and surface modification on the adsorption performance of methylene blue and Cu2+ in mesoporous silica. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 539**,** 154-162.

Gervas, C., Mubofu, E. B., Mdoe, J. E. & Revaprasadu, N., 2016. Functionalized mesoporous organo-silica nanosorbents for removal of chromium (III) ions from tanneries wastewater. Journal of Porous Materials. 23**,** 83-93.

Gu, D., Zhang, F., Shi, Y., Zhang, F., Wu, Z., Deng, Y., Zhang, L., Tu, B. & Zhao, D., 2008. A "teardown" method to create large mesotunnels on the pore walls of ordered mesoporous silica. Journal of colloid and interface science. 328**,** 338-343.

Gunathilake, C., Kadanapitiye, M. S., Dudarko, O., Huang, S. D. & Jaroniec, M., 2015. Adsorption of lead ions from aqueous phase on mesoporous silica with P-containing pendant groups. ACS applied materials and interfaces. 7**,** 23144-23152.

Gupta, V. K., Nayak, A., Bhushan, B. & Agarwal, S., 2015. A critical analysis on the efficiency of activated carbons from low-cost precursors for heavy metals remediation. Critical Reviews in Environmental Science and Technology. 45**,** 613-668.

Han, Y., Chen, J., Gu, X. & Chen, J., 2021. Adsorption of multi-bivalent heavy metal ions in aqueous solution onto aminopropyl-functionalized MCM-48 preparation by co-condensation. Separation Science and Technology. 56**,** 1819-1829.

He, R., Wang, Z., Tan, L., Zhong, Y., Li, W., Xing, D., Wei, C. & Tang, Y., 2018. Design and fabrication of highly ordered ion imprinted SBA-15 and MCM-41 mesoporous organosilicas for efficient removal of Ni2+ from different properties of wastewaters. Microporous and mesoporous materials. 257**,** 212-221.

Heidari, A., Younesi, H. & Mehraban, Z., 2009. Removal of Ni (II), Cd (II), and Pb (II) from a ternary aqueous solution by amino functionalized mesoporous and nano mesoporous silica. Chemical Engineering Journal. 153**,** 70-79.

Huang, J., Ye, M., Qu, Y., Chu, L., Chen, R., He, Q. & Xu, D., 2012. Pb (II) removal from aqueous media by EDTA-modified mesoporous silica SBA-15. Journal of colloid and interface science. 385**,** 137-146.

Huang, Z. & Che, S., 2015. Fabrication of mesostructured silica materials through co-structure-directing route. Bulletin of the Chemical Society of Japan. 88**,** 617-632.

Idris, S. A., Alotaibi, K., Peshkur, T. A., Anderson, P., Gibson, L. T. J. J. O. C. & Science, I., 2012. Preconcentration and selective extraction of chromium species in water samples using amino modified mesoporous silica. Journal of colloid and interface science. 386**,** 344-349.

Idris, S. A., Davidson, C. M., Mcmanamon, C., Morris, M. A., Anderson, P. & Gibson, L. T., 2011. Large pore diameter MCM-41 and its application for lead removal from aqueous media. Journal of hazardous materials. 185**,** 898-904.

Jadhav, S. A., Garud, H. B., Thoravat, S. S., Patil, V. S., Shinde, P. S., Burungale, S. H. & Patil, P. S., 2021. Synthesis and testing of functional mesoporous silica nanoparticles for removal of Cr (VI) ions from water. Biointerface Res. Appl. Chem. 11**,** 8599-8607.

Jang, E.-H., Pack, S. P., Kim, I. & Chung, S., 2020. A systematic study of hexavalent chromium adsorption and removal from aqueous environments using chemically functionalized amorphous and mesoporous silica nanoparticles. Scientific reports. 10**,** 1-20.

Jeong, E.-Y., Ansari, M. B., Mo, Y.-H. & Park, S.-E., 2011. Removal of Cu (II) from water by tetrakis (4-carboxyphenyl) porphyrin-functionalized mesoporous silica. Journal of hazardous materials. 185**,** 1311-1317.

Jia, W., Xu, H., Yang, Q., Ren, S. & Wang, J., 2019. Synthesis of anionic gemini surfactant-templated mesoporous silica nanoparticles and its adsorption application for Pb2+. Journal of Dispersion Science and Technology.

Jiang, Y., Gao, Q., Yu, H., Chen, Y. & Deng, F., 2007. Intensively competitive adsorption for heavy metal ions by PAMAM-SBA-15 and EDTA-PAMAM-SBA-15 inorganic–organic hybrid materials. Microporous and Mesoporous Materials. 103**,** 316-324.

Lachowicz, J. I., Delpiano, G. R., Zanda, D., Piludu, M., Sanjust, E., Monduzzi, M. & Salis, A., 2019. Adsorption of Cu2+ and Zn2+ on SBA-15 mesoporous silica functionalized with triethylenetetramine chelating agent. Journal of Environmental Chemical Engineering. 7**,** 103205.

Lam, K. F., Chen, X., Mckay, G. & Yeung, K. L., 2008. Anion effect on Cu2+ adsorption on NH2-MCM-41. Industrial and engineering chemistry research. 47**,** 9376-9383.

Lee, J., Kim, J.-H., Choi, K., Kim, H.-G., Park, J.-A., Cho, S.-H., Hong, S. W., Lee, J.-H., Lee, J. H. & Lee, S., 2018. Investigation of the mechanism of chromium removal in (3-aminopropyl) trimethoxysilane functionalized mesoporous silica. Scientific reports. 8**,** 1-11.

Lei, D., Zheng, Q., Wang, Y. & Wang, H., 2015. Preparation and evaluation of aminopropyl-functionalized manganese-loaded SBA-15 for copper removal from aqueous solution. Journal of Environmental Sciences. 28**,** 118-127.

Li, M., Zhang, C., Yang, X.-L. & Xu, H.-B., 2013. Controllable synthesis of hollow mesoporous silica nanoparticles templated by kinetic self-assembly using a gemini surfactant. RSC advances. 3**,** 16304-16307.

Liu, A., Hidajat, K., Kawi, S. & Zhao, D., 2000. A new class of hybrid mesoporous materials with functionalized organic monolayers for selective adsorption of heavy metal ions. Chemical Communications**.** 1145-1146.

Marjani, A. & Mohammadi, R. K., 2021. Synthesis of novel adsorbent based on tetrasulfide-functionalized fibrous silica KCC-1 for removal of Hg (II) cations. Scientific Reports. 11**,** 1-12.

Mohammadnezhad, G., Moshiri, P., Dinari, M. & Steiniger, F., 2019. In situ synthesis of nanocomposite materials based on modified-mesoporous silica MCM-41 and methyl methacrylate for copper (II) adsorption from aqueous solution. Journal of the Iranian Chemical Society. 16**,** 1491-1500.

**Correspondence: imalka@sjp.ac.lk*

Munday, R., 1989. Toxicity of thiols and disulphides: involvement of free-radical species. Free Radical Biology and Medicine. 7**,** 659-673.

Owalude, S. O. & Tella, A. C., 2016. Removal of hexavalent chromium from aqueous solutions by adsorption on modified groundnut hull. Beni-suef university journal of basic and applied sciences, 5**.** 377-388.

Parida, K. & Dash, S. K., 2010. Adsorption of Cu2+ on spherical Fe-MCM-41 and its application for oxidation of adamantane. Journal of hazardous materials. 179**,** 642-649.

Parida, K., Mishra, K. G. & Dash, S. K., 2012. Adsorption of toxic metal ion Cr (VI) from aqueous state by TiO2-MCM-41: Equilibrium and kinetic studies. Journal of hazardous materials. 241**,** 395-403.

Putz, A.-M., Ciopec, M., Negrea, A., Grad, O., Ianăşi, C., Ivankov, O. I., Milanović, M., Stijepović, I. & Almásy, L., 2021. Comparison of structure and adsorption properties of mesoporous silica functionalized with aminopropyl groups by the co-condensation and the post grafting methods. Materials. 14**,** 628.

Qasem, N. A., Mohammed, R. H. & Lawal, D. U., 2021. Removal of heavy metal ions from wastewater: A comprehensive and critical review. Npj Clean Water. 4**,** 1-15.

Qdais, H. A. & Moussa, H., 2004. Removal of heavy metals from wastewater by membrane processes: a comparative study. Desalination. 164**,** 105-110.

Rabie, A. M., Abd El-Salam, H., Betiha, M., El-Maghrabi, H. & Aman, D., 2019. Mercury removal from aqueous solution via functionalized mesoporous silica nanoparticles with the amine compound. egyptian Journal of Petroleum. 28**,** 289-296.

Raei, B., Barekat, A. & Shariyatinia, H., 2019. Removal of Ni (II) from aqueous solution using modified MCM-41 nano-adsorbents. Advances in Environmental Technology. 5**,** 157-169.

Rath, D., Rana, S. & Parida, K., 2014. Organic amine-functionalized silica-based mesoporous materials: an update of syntheses and catalytic applications. RSC advances. 4**,** 57111-57124.

Sarafraz, H., Minuchehr, A., Alahyarizadeh, G. & Rahimi, Z., 2017. Synthesis of enhanced phosphonic functional groups mesoporous silica for uranium selective adsorption from aqueous solutions. Scientific reports. 7**,** 1-12.

Showkat, A. M., Zhang, Y.-P., Kim, M.-S., Gopalan, A. I., Reddy, K. R. & Lee, K.-P., 2007. Analysis of heavy metal toxic ions by adsorption onto amino-functionalized ordered mesoporous silica. Bulletin of the Korean Chemical Society. 28**,** 1985-1992.

Soltani, R., Dinari, M. & Mohammadnezhad, G., 2018. Ultrasonic-assisted synthesis of novel nanocomposite of poly (vinyl alcohol) and amino-modified MCM-41: a green adsorbent for Cd (II) removal. Ultrasonics Sonochemistry. 40**,** 533-542.

Soltani, R., Marjani, A., Hosseini, M. & Shirazian, S., 2020. Synthesis and characterization of novel N-methylimidazolium-functionalized KCC-1: A highly efficient anion exchanger of hexavalent chromium. Chemosphere. 239**,** 124735.

Soltani, R., Marjani, A., Moguei, M. R. S., Rostami, B. & Shirazian, S., 2019. Novel diamino-functionalized fibrous silica submicro-spheres with a bimodal-micro-mesoporous network: Ultrasonic-assisted fabrication, characterization, and their application for superior uptake of Congo red. Journal of Molecular Liquids. 294**,** 111617.

Tapaswi, P. K., Moorthy, M. S., Park, S. S. & Ha, C.-S., 2014. Fast, selective adsorption of Cu2+ from aqueous mixed metal ions solution using 1, 4, 7-triazacyclononane modified SBA-15 silica adsorbent (SBA-TACN). Journal of Solid State Chemistry. 211**,** 191-199.

Upadhyay, U., Sreedhar, I., Singh, S. A., Patel, C. M. & Anitha, K., 2021. Recent advances in heavy metal removal by chitosan based adsorbents. Carbohydrate Polymers. 251**,** 117000.

Verbych, S., Hilal, N., Sorokin, G. & Leaper, M., 2005. Ion exchange extraction of heavy metal ions from wastewater. Separation science and technology. 39**,** 2031-2040.

Wang, B., Zhou, Y., Li, L., Xu, H., Sun, Y. & Wang, Y., 2018. Novel synthesis of cyano-functionalized mesoporous silica nanospheres (MSN) from coal fly ash for removal of toxic metals from wastewater. Journal of hazardous materials. 345**,** 76-86.

Wang, C., Lin, G., Xi, Y., Li, X., Huang, Z., Wang, S., Zhao, J. & Zhang, L., 2020. Development of mercaptosuccinic anchored MOF through one-step preparation to enhance adsorption capacity and selectivity for Hg (II) and Pb (II). Journal of Molecular Liquids. 317**,** 113896.

Wongsakulphasatch, S., Kiatkittipong, W., Saiswat, J., Oonkhanond, B., Striolo, A. & Assabumrungrat, S., 2014. The adsorption aspect of Cu2+ and Zn2+ on MCM-41 and SDS-modified MCM-41. Inorganic Chemistry Communications. 46**,** 301-304.

Wu, S., Li, F., Xu, R., Wei, S. & Li, G., 2010. Synthesis of thiol-functionalized MCM-41 mesoporous silicas and its application in Cu (II), Pb (II), Ag (I), and Cr (III) removal. Journal of Nanoparticle Research. 12**,** 2111-2124.

Wu, Y., Yang, S., Zhang, M., Aierken, A. & Wu, Y., 2015. Abatement of Cr (VI) and As (III) by MnO2 loaded MCM-41 in wastewater treatment. Korean Journal of Chemical Engineering. 32**,** 1667-1677.

Xue, X. & Li, F., 2008. Removal of Cu (II) from aqueous solution by adsorption onto functionalized SBA-16 mesoporous silica. Microporous and Mesoporous Materials. 116**,** 116-122.

Yan, X., Meng, J., Hu, X., Feng, R. & Zhou, M., 2019. Synthesis of thiol-functionalized mesoporous silica nanoparticles for adsorption of Hg2+ from aqueous solution. Journal of Sol-Gel Science and Technology. 89**,** 617-622.

Yang, S., Chen, S., Fan, J., Shang, T., Huang, D. & Li, G., 2019. Novel mesoporous organosilica nanoparticles with ferrocene group for efficient removal of contaminants from wastewater. Journal of colloid and interface science. 554**,** 565-571.

Yang, X. & Liu, H., 2018. Ferrocene-Functionalized Silsesquioxane-Based Porous Polymer for Efficient Removal of Dyes and Heavy Metal Ions. Chemistry–A European Journal. 24**,** 13504-13511.

Yantasee, W., Lin, Y., Fryxell, G. E., Busche, B. J. & Birnbaum, J. C., 2003. Removal of heavy metals from aqueous solution using novel nanoengineered sorbents: self-assembled carbamoylphosphonic acids on mesoporous silica. Separation Science and Technology. 38**,** 3809-3825.

Yokoi, T., Yoshitake, H. & Tatsumi, T., 2004. Synthesis of amino-functionalized MCM-41 via direct co-condensation and post-synthesis grafting methods using mono-, di-and tri-amino-organoalkoxysilanes. Journal of Materials Chemistry. 14**,** 951-957.

Yokoi, T., Yoshitake, H., Yamada, T., Kubota, Y. & Tatsumi, T., 2006. Amino-functionalized mesoporous silica synthesized by an anionic surfactant templating route. Journal of Materials Chemistry. 16**,** 1125-1135.

Yu, N., Wu, K. & Tao, L., 2021. Synchronous reduction-fixation of reducible heavy metals from aqueous solutions: Application of novel mesoporous MFT/SBA-15 composite materials. Chemosphere. 276**,** 130112.

Zhang, L., Song, F., Wu, Y., Cheng, L., Qian, J., Wang, S., Chen, Q. & Li, Y., 2018. A novel amino and carboxyl functionalized mesoporous silica as an efficient adsorbent for nickel (II). Journal of Chemical and Engineering Data. 64**,** 176-188.

**Correspondence: imalka@sjp.ac.lk*

Zhang, Y., Cao, X., Sun, J., Wu, G., Wang, J. & Zhang, D., 2020. Synthesis of pyridyl Schiff base functionalized SBA-15 mesoporous silica for the removal of Cu (II) and Pb (II) from aqueous solution. Journal of Sol-Gel Science and Technology. 94**,** 658-670.

7 Acknowledgment

Department of Chemistry, Faculty of Applied Sciences, University of Sri Jayewardenepura, Gangodawila, Nugegoda, Sri Lanka.