

A MINI REVIEW ON SPOROPOLLENIN-BASED MATERIALS FOR REMOVAL OF HEAVY METAL IONS FROM AQUEOUS SOLUTION

(Ulasan Mini Ke Atas Bahan Berasaskan Sporopollenin untuk Penyingkiran Ion Logam Berat dari Larutan Aqueus)

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Abstract

The use of sporopollenin-based materials as adsorbents in addressing environmental problems such as in removal of heavy metals from aqueous environment has received limited attention despite its remarkable physical and chemical properties that guaranteed its great potential for this application. This mini-review provides up-to-date information on the research and development of sporopollenin-based materials for the treatment of toxic heavy metals contaminated aqueous environments. Conventional techniques for heavy-metals removal from aqueous environment are discussed; limitations and advantages of these techniques are highlighted. Sporopollenin-based materials were found to be good adsorbents in control and remediation of heavy-metal ions in wastewater, but considering its characteristics, the full potentials of sporopollenin for this application is yet to be fully harnessed.

Keywords: sporopollenin, adsorbent, aqueous solution, heavy metals, environment

Abstrak

Penggunaan bahan berasaskan sporopollenin sebagai penyerap dalam menyelesaikan masalah alam sekitar seperti penyingkiran logam berat dari larutan akueus telah mendapat perhatian terhad walaupun sifat fizikal dan kimianya yang luar biasa yang menjamin potensi yang besar untuk aplikasi ini. Ulasan mini ini memberikan maklumat terkini tentang penyelidikan dan pembangunan bahan berasaskan sporopollenin untuk merawat persekitaran akueus yang dicemari logam berat bertoksik. Teknik konvensional untuk penyingkiran logam berat dari persekitaran akueus dibincangkan; kelemahan serta kelebihan teknik ini diserlahkan. Bahan berasaskan sporopollenin didapati adalah penyerap yang baik dalam kawalan dan pemulihan ion logam berat dalam air kumbahan tetapi mempertimbangkan cirinya, potensi keseluruhan sporopollenin untuk aplikasi ini masih belum dimanfaatkan sepenuhnya.

Kata kunci: sporopollenin, penyerap, larutan akueus, logam berat, alam sekitar

Introduction

High level of heavy metals (HMs) contaminated water resource due to industrialization and human activities constitute a serious threat to the environment and public health [1]. Heavy metals like nickel, lead, chromium, arsenic, cadmium, mercury and copper, are hazardous to organisms even at very small concentrations. These metal ions accumulation in human system causes severe health problems such as cancers, bone softening, kidney failure, malfunction of nervous system and other serious illnesses [2]. Nowadays, adsorption technique through complexation or ion exchange mechanism is popularly used to mitigate metal ions toxicity in contaminated aqueous environment. Materials such as biomaterials, silica gel, activated carbon and resins [1] have been used for this purpose. However, the improvement of adsorbent's selectivity for heavy metals ions, involves the introduction of special functional groups with high affinity for metal ions onto the polymer matrix of the adsorbent [3]. In this case, the structure and chemical composition of the adsorbent as a supporting material plays significant role the overall efficiency of the modified material or adsorbent.

One of such materials that can be used as adsorbent and excellent support is *Lycopodium clavatum* (sporopollenin, Sp). Sp is a highly resistant bio-macromolecule that occurs in nature as a component of the outer wall of spores and pollen which is resistant to attacks by mineral acids and alkalis. It can survive in geological strata over millions of years with full retention of its morphological characteristics, these suggest good stability of Sp at extreme conditions [4]. However, the detailed chemical structure of the Sp is yet unknown but it has stable cross-linked aromatic structure containing carbon, hydrogen, and oxygen in a stoichiometry of $C_{90}H_{144}O_{27}$ [5]. In addition, its main functional group is hydroxyl functional groups available for modification in large quantities. Thus, the hydroxyl group serves as anchoring sites for metal ion complexation as well as addition of desired surface functional groups and other materials with high affinity

for metal ion [5]. However, literature search suggested that, studies on Sp-based materials for the removal of metal ions are quite few. The objective of this mini review is to report for the first time, the synthesis and application of different Sp-based materials so far being used for the removal of heavy-metal ions from aqueous solution in order to provide insights of what need to be done to further harness its full potentials in removing heavy metal ions from contaminated aqueous environment.

Heavy metals

HMs naturally occur as part of the earth's crust, in rocks or soils, and are regarded as any dense metal with atomic weights of 63.5 - 200.6 Dalton, and a specific gravity above 5 g/mL [6, 7]. HMs includes cadmium, antimony, nickel, arsenic, lead, copper, cobalt, uranium, chromium, zinc, selenium, thallium and mercury [8]. Most of these heavy metals are discharged into the aquatic environment as domestic wastes or industrial effluents, causing water pollution [9]. Heavy metals are not degradable, thus tend to persist in environment, as a serious threat to public health once discharged.

Arsenic contaminated drinking water is a health risks to approximately 150 million people globally [10]. Cadmium has been identified as a potent carcinogen, its toxicity may also cause bone defects (osteomalacia and osteoporosis) [11]. Exposure to cadmium may also cause diseases of reproductive organs, lungs, kidneys and liver [12, 13]. Lead poisoning causes gastrointestinal diseases, central nervous system diseases, constipation and abdominal pains [14]. Mercury exposure may cause chest pain, impairment of pulmonary function, impairment of the kidney and dyspnoea [15]. Mercury accumulates in the brain, causing neurological and psychiatric effects [16, 17]. Chromium is found in the environment as Cr(III) and Cr(VI). Exposure to chromium causes lung cancers, skin irritation, kidney and liver damage [18, 19]. Considering the hazardous effects of these heavy metals, the World Health Organization (WHO) and the

United States Environmental Protection Agency (US EPA) have set maximum permissible limits (MPL) for metals in drinking water (Table 1). As a comparison, the MPL for Ministry of Health (MOH) Malaysia is also given.

Techniques for removing heavy metal ions from aqueous solution

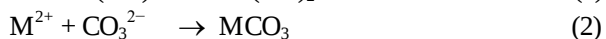
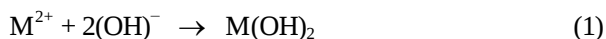
Several methods are used for the removal of heavy metals ions from aqueous environments; the most widely used are chemical precipitation, ion exchange and adsorption [23].

Chemical precipitation

Precipitation is a chemical process in which soluble substances in a solution reacts chemically with certain suitable reagents to form insoluble solid precipitate. Metal precipitation can occur either through the addition of sodium hydroxide or lime (hydroxide precipitation) [24-26], addition of calcium or sodium carbonate (carbonate precipitation) [25, 26] or addition of sulfide ions (sulphide precipitation) [26].

Chemical precipitation is widely applied to remove to heavy metals from industrial effluents [23, 27, 28]. However, it was observed that removing metal ions through sulphide precipitation is more efficient compared to hydroxide and carbonate precipitation [3].

Equations 1-3 presents the conceptual mechanism of heavy-metal removal using chemical precipitation.



where M^{2+} is dissolved metal ions, OH^{-} is hydroxide, CO_3^{2-} is carbonate and S^{2-} is sulphide, while the precipitants are the insoluble metal hydroxide ' $M(OH)_2$ ', carbonate ' MCO_3 ' and sulphide ' MS ', respectively.

In chemical precipitation, the metal ions usually precipitated from solution in the form of insoluble hydroxides, carbonates and sulphides by pH adjustment of the solution to basic condition of pH (9–11). Materials such as lime and limestone are often used as precipitants for pH adjustment to the basic range [29, 30]. Lime and limestone are cost effective and available. Recently, lime was use alongside milk casein for precipitation and form separation of heavy metals from mining wastewater. The milk casein functioned as a collector and a frother for foam separation in this system [31]. However, limitations of chemical precipitation involve the use of large volume of chemicals to reduce metals to an acceptable environmental limits for discharge, sludge production, environmental problems associated with sludge disposal and slow metal precipitation [30].

Table 1. Maximum permissible limit (MPL) of seven heavy metals in drinking water [20-22]

Heavy Metals	MPL (mg/L)		
	USEPA	WHO	MOH Malaysia
Lead	0.015	0.005	0.01
Cadmium	0.005	0.005	0.003
Mercury	0.002	0.001	0.001
Arsenic	0.01	0.01	0.01
Chromium	0.1	0.05	0.05
Nickel	0.04	-	0.02
Selenium	0.05	0.01	0.01

Ion exchange

Removing heavy metals through ion exchange involves the transfer of ions in the aqueous solution unto a solid matrix, which as a result, releases ions of a different type but of the same charge [32]. In addition to synthetic organic ion-exchange resins such as Purolite C100 [33], Lewatit TP207 and Lewatit TP208 [34], 2,4- DHBEDF [35], Chelex-100 and Amberlite IRC748 [36] and C160-Purolite [37]. Other commonly used materials for ion exchange are zeolites, which have good cation-exchange ability [38, 39]. Alvarez et al. [40] studied the efficiency of natural zeolite (clinoptilolite) and synthetic zeolites (NaP1) to remove heavy metals from wastewater. It was found that synthetic zeolite has higher efficiency in removing heavy metals from wastewater compared to natural zeolite.

Natural zeolites effectively removed heavy metal from aqueous solution [41] and metal finishing wastewater [42]. Furthermore, modified natural zeolite such Fe(III)-zeolite [43, 44] and zeolite-alginate composite [45] have also been reported as ion-exchange materials for removal of heavy metals from industrial wastewater. On the other hand, synthetic zeolite prepared *via* alkali fusion of coal fly ash, followed by thermal treatment to improve the zeolite ion exchange ability to remove heavy metal from mineral and metal processing wastewater has been reported [46]. Recently, thermally treated zeolite showed good performance in removing heavy metal ions from wastewater with high thermal stability and retention of metal ions during ion exchange [47]. Thermal treatment is a promising technique to improve the performance of zeolites. The advantages of ion-exchange over chemical precipitation method are selectivity and less sludge volume are produced. However, its limitations are that the process cannot effectively treat concentrated solutions [23, 48] and incur high operational cost [48].

Adsorption

Adsorption is a promising and convenient technique for removing heavy metals ions from contaminated water. Adsorption involves the transfer of ions from solution

to adsorbent surface then becomes bounded by either physical or chemical interactions [49]. Many materials have been reported as adsorbents for removal of metal ions from aqueous environments such as carbon nanomaterials (CNM) [50], multiwall carbon nanotubes (MWCNTs) [51], activated carbon (AC) [52], modified polypyrrole films [53], poly(-acrylamide) grafted on modified Fe₃O₄ [54], *Tinospora cordifolia* [55], algae waste biomass [56], modified sewage sludge [57], *Bauhini purpurea* pods [58], Chestnut buds [59], lignin/corn cob biochar [60], activated carbon of *Typha angustifolia* [61], coal fly ash-nZVI [62], synthetic mineral [63], poly(methacrylamide) grafted crosslinked chitosan [64], silica-cyanopropyl magnetic GO (MGO/SiO₂-CN) [65], graphene oxide functionalized with dithiocarbamate [66], graphene oxide (GO) [67] and Sp [68]. Adsorption has several advantages over various methods of removing metal ions from aqueous solution such as the possibility to modify and improve the properties of adsorbent, selectivity, reusability and cost effectiveness. Furthermore, due to high adsorption capacities of adsorbents, this process is suitable for the treatments of high concentrated heavy metals contaminated aqueous environment.

Sporopollenin-based materials for metal ions removal from aqueous environment

Unmodified Sp was used as adsorbent to remove Cu(II), Pb(II) and Cd(II) from aqueous solution. Adsorption capacities of 0.0195, 0.0411 and 0.0146 mmol/g for Cu(II), Pb(II) and Cd(II), respectively at optimum conditions [68]. Modification is necessary on the Sp, in order to improve its adsorption efficiency and harness its full potential in remediating heavy metals contaminated aqueous environments. In a related study, Murat et al. [69] used pretreated sporopollenin (PSP) biomass to remove Pb(II) and Cu(II) from water through batch biosorption technique and optimized using response surface methodology. Although this study reports only pretreatment not chemical modification with improved binding sites, Sp was pretreated using concentrated nitric acid in order to improve its metal affinity. However, Sp being a tough

biomaterial with physical, chemical stability and complex structure is likely to suffer from long diffusion path through solid particles. Thus, concentrated nitric acid was used to reduce the toughness and improve the porous nature of Sp for the metal ions to easily access the binding sites on Sp. The maximum adsorption capacity, $q_{\max}$ of PSp was 6.10 and 4.84 mg/g for Pb(II) and Cu(II), respectively.

Dithiocarbamated-Sp (DTC-Sp) was synthesised as adsorbent for removal of Cu(II), Pb(II) and Cd(II) from aqueous solution. The synthesis steps involved grafting of ethylenediamine (DAE) groups onto the Sp network. Furthermore, addition of carbon disulfide converted the amine groups to dithiocarbamates. The DTC-Sp attained a $q_{\max}$ of 0.2734, 0.4572 and 0.0631 mmol/g for Cu(II), Pb(II) and Cd(II) metal ions, respectively [70]. DTC-Sp showed 1,320%, 1,012% and 332% improvements in sorption capacity for Cu(II), Pb(II) and Cd(II) respectively, compared to unmodified Sp, probably due to the presence of sulphur in dithiocarbamates, which improved the affinity of the adsorbent for these metal ions.

Sener et al. [71] reported magnetic nanoparticles modified Sp (Fe_3O_4 -Sp) as biosorbent for removal of Pb(II) from aqueous solution with $q_{\max}$ of 22.7 mg/g. Modification of Sp with Fe_3O_4 was to facilitate separation after adsorption via the application of external magnet, without going through the tedious and time consuming filtration and centrifugation processes. However, Fe_3O_4 -Sp showed superior $q_{\max}$ for Pb(II) (272% higher) compared to PSp. Recently, 1-(2-hydroxyethyl) piperazine magnetic nanoparticles-Sp (MNPs-Sp-HEP) was synthesized via modification of Sp spores with 3-cyanopropyltrimethoxysilane, then functionalized with 1-(2-hydroxyethyl) piperazine (Sp-HEP). The magnetic nanoparticles were then introduced, to modify the Sp-HEP to produce MNPs-Sp-HEP (Figure 1).

The MNPs-Sp-HEP was applied as adsorbent for the removal of Pb(II) and As(III) from aqueous solution. This adsorbent shows more selectivity for As(III) which attained $q_{\max}$ of 13.36 and 69.85 mg/g for Pb(II)

and As(III), respectively in aqueous media [72], showing 119% increment in Pb(II) $q_{\max}$ compared to PSp, but 70% less Pb(II) $q_{\max}$ compared to Fe_3O_4 -Sp. MNPs-Sp-HEP was easily separated from aqueous solution with the help of external magnet. This could be due to the competition of Pb(II) and As(III) for the limited active sites on MNPs-Sp-HEP. Thus, affecting its performance on Pb(II) adsorption.

Ersoz et al. [73] conducted a study to remove Zn(II), Cd(II) and As(III) from water using carboxylated-diaminoethyl modified Sp (DAEC-Sp) and bis-diaminoethyl-glyoxime Sp (bDAEG-Sp). These Sp-based materials possessing oxime and carboxylic acid functionality were synthesized via the reaction of diamino-Sp with bromoacetic acid and dichloro-antiglyoxime respectively. The $q_{\max}$ of DAEC-Sp was 1.801, 1.500 and 1.119 mmol/g for Zn(II), Cd(II) and As(III), respectively while bDAEG-Sp attained $q_{\max}$ of 1.855, 1.261 and 1.127 mmol/g for Zn(II), Cd(II) and As(III), respectively at solution pH of 6 and 50 °C. DAEC-Sp and bDAEG-Sp showed 2,277% and 1898% higher $q_{\max}$ for Cd(II) respectively, compared to DTC-Sp. However, 10.174% and 8.537% increment in Cd(II) $q_{\max}$ was achieved for DAEC-Sp and bDAEG-Sp compared to unmodified-Sp. Furthermore, there was not much difference (0.71%) in $q_{\max}$ of DAEC-Sp and bDAEG-Sp for As(III), this suggested that, the materials have almost similar sorption affinity for As(III).

Gode and Pehlivan [4] also employed b-DAEG-Sp and carboxylated epi-chlorohydrine-Sp (CEP-Sp) to remove Cr(III) from aqueous solution. b-DAEG-Sp attained a $q_{\max}$ of 1.23 mmol/g while CEP-Sp attained a high $q_{\max}$ of 133 mmol/g. Based on these findings, it can be deduced that, CEP is a better material to modify Sp compared to b-DAEG. Idris and Gulsin [74] reported chitosan modified Sp (chitosan-Sp) as hybrid bio-macromolecules adsorbent for metal ions. This material was prepared via cross-linking of chitosan with Sp. However, comparison was made on the sorption performance of chitosan-Sp and plain chitosan for Cu(II), Cd(II), Cr(III), Ni(II) and Zn(II) ions.

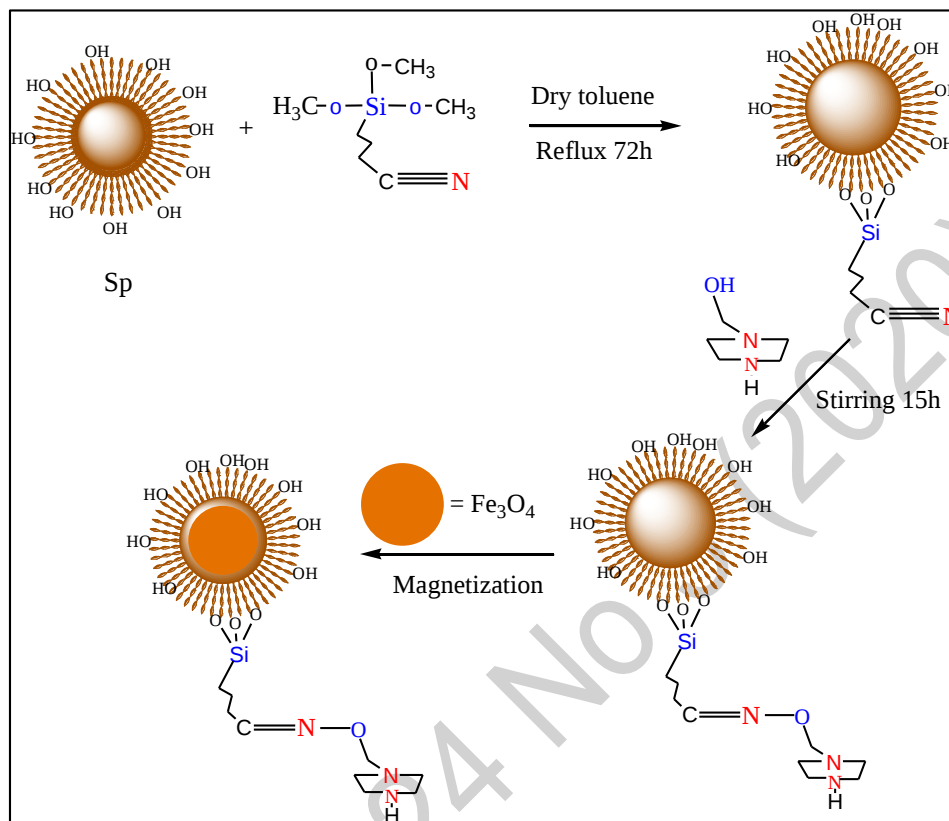


Figure 1. Schematic routes for the preparation of 1-(2-hydroxyethyl) piperazine-functionalized magnetic-Sp (MNP-Sp-HEP)

Chitosan-Sp attained $q_{\max}$ of 1.34, 0.77, 0.99, 0.58 and 0.71 mmol/g for Cu(II), Cd(II), Cr(III), Ni(II), and Zn(II) ions, respectively. Plain chitosan attained $q_{\max}$ for Cu(II): 1.46, Cr(III): 1.16, Cd(II): 0.15, Ni(II): 0.81 and Zn(II): 0.25 mmol/g. This showed that, Sp enhanced the affinity and sorption capacity of the chitosan for Cd(II) and Zn(II) by 413% and 184% respectively. Thus, chitosan-Sp can be used in Cd(II) and Zn(II) ions removal. Furthermore, Sp immobilized E-4-((2-hydroxyphenylimino) methyl) benzoic acid (Sp-HPBA) adsorbent, attained $q_{\max}$ of only 0.043, 0.036 and 0.039 mmol/g for Cu(II), Ni(II) and Co(II), respectively, in aqueous solution [75]. In a related study, glutaraldehyde immobilized sporopollenin (GA-Sp) synthesized *via* sequential treatment of Sp with glutaraldehyde attained a $q_{\max}$ of 0.042, 0.143 and 0.130 mmol/g for Cu(II), Zn(II) and Co(II) respectively

[76]. Sp-HPBA showed only 2.4% increment in Cu(II) $q_{\max}$ value compared to GA-Sp, but, the $q_{\max}$ of GA-Sp for Co(II) improved by 233% compared to Sp-HPBA.

Gode and Pehlivan [4] also employed b-DAEG-Sp and carboxylated epi-chlorohydrine-Sp (CEP-Sp) to remove Cr(III) from aqueous solution. b-DAEG-Sp attained a $q_{\max}$ of 1.23 mmol/g while CEP-Sp attained a high $q_{\max}$ of 133 mmol/g. Based on these findings, it can be deduced that, CEP is a better material to modify Sp compared to b-DAEG. Idris and Gulcin [74] reported chitosan modified Sp (chitosan-Sp) as hybrid bio-macromolecules adsorbent for metal ions. This material was prepared *via* cross-linking of chitosan with Sp. However, comparison was made on the

sorption performance of chitosan-Sp and plain chitosan for Cu(II), Cd(II), Cr(III), Ni(II) and Zn(II) ions.

p-tert-butylcalix[4]-aza-crown (CAC) immobilized Sp was used as a sorbent for the removal of selected heavy metals from aqueous media. Sp was initially functionalized with 3-chloropropyltrimethoxysilane (CPTS) to produce chloro-Sp (Sp-Cl). The Sp-Cl was further reacted with CAC to form the sorbent (Sp-Cl-CAC). The $q_{\max}$ of Sp-Cl-CAC for Zn(II), Pb(II) and Cu(II) were 0.14, 0.07, and 0.07 mmol/g, at pH 5.5 for Zn(II) and 5.0 for Cu(II) and Pb(II) [77]. Sp-Cl-CAC showed more affinity for Cu(II) compared to the earlier mentioned Sp-HPBA and GA-Sp adsorbents. Another calix[4]arene modified Sp, *p*-tert-butylcalix[4]arene-Sp (*p*-t-bCalix-Sp) was used for the removal of Cr(VI) from aqueous media. Calix-Sp was synthesised *via* the immobilization of dihydrazine amide derivative of *p*-tert-butylcalix[4]arene onto the Sp. Using batch adsorption technique, the sorption of Cr(VI) was pH dependent and optimum pH was 1.5. The $q_{\max}$ of

Cr(IV) sorption onto Calix-Sp was found to be 0.54 mmol/g [78], *p*-t-bCalix-Sp appeared to be the only Sp-based sorbent so far used for the sorption of Cr(IV).

Recently, 3-aminopropyltrimethoxysilane functionalized Sp based silica coated GO (GO@SiO₂-MSp@SiO₂-NH₂) was used as hybrid adsorbent for removal of Pb(II) from aqueous environment, which attained $q_{\max}$ of 323.5 mg/g [79]. Figure 2 illustrates the synthesis of GO@SiO₂-MSp@SiO₂-NH₂. The adsorbent showed significantly higher sorption capacity of 1,325% and 2,321% compared to Fe₃O₄-Sp and MNps-Sp-HEP respectively. This is probably due to the modification of the Sp with 3-aminopropyltrimethoxysilane and GO, which improved the sorption affinity of GO@SiO₂-MSp@SiO₂-NH₂ towards Pb(II). Table 2 shows a summary of the reviewed Sp-based sorbents and their $q_{\max}$ values for metal ions.

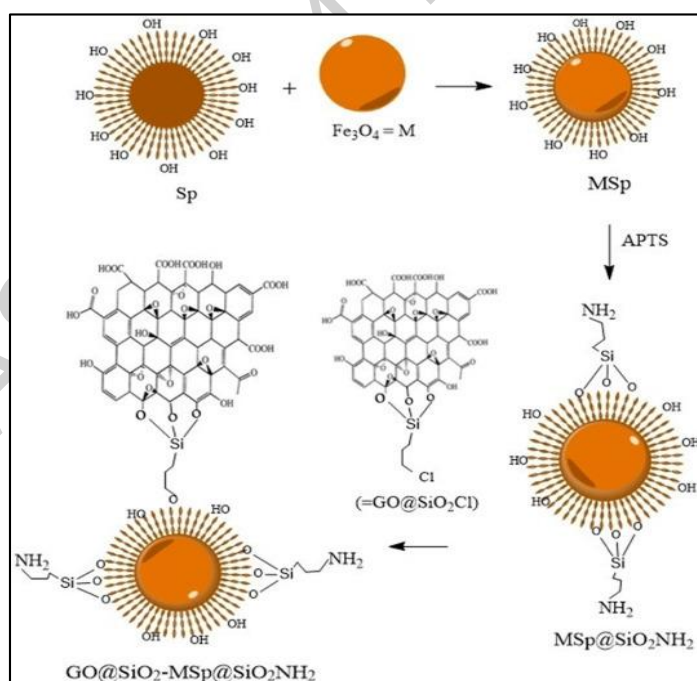


Figure 2. Schematic routes for the preparation of GO@SiO₂-MSp@SiO₂-NH₂ [79]

Table 2. Summary of Sp-based sorbents for removal of metal ions

Sorbent	Metal Ion	$q_{\max}$ (mmol/g)	References
Sp	Cu(II)	0.0195	68
	Pb(II)	0.0411	
	Cd(II)	0.0146	
PSp	Pb(II)	6.10	69
	Cu(II)	4.84	
DTC-Sp	Cu(II)	0.2734	70
	Pb(II)	0.4572	
	Cd(II)	0.0631	
Fe ₃ O ₄ -Sp	Pb(II)	22	71
MNps-Sp-HEP	Pb(II)	13.36	72
	As(III)	69.85	
DAEC-Sp	Zn(II)	1.801	73
	Cd(II)	1.500	
	As(III)	1.119	
bDAEC-Sp	Zn(II)	1.855	73
	Cd(II)	1.261	
	As(III)	1.127	
	Cr(III)	1.23	
CEP-Sp	Cr(III)	133	4
Chitosan-Sp	Cd(II)	0.77	74
	Zn(III)	0.71	
Sp-HPBA	Cu(II)	0.043	75
	Ni(II)	0.036	
	Co(II)	0.039	
GA-Sp	Cu(II)	0.042	76
	Ni(II)	0.143	
	Co(II)	0.130	
Sp-Cl-CAC	Zn(II)	0.14	77
	Pb(II)	0.07	
	Cu(II)	0.07	
<i>p-t</i> -bCalix-Sp	Cr(VI)	0.54	78
GO@SiO ₂ -MSP@SiO ₂ -NH ₂	Pb(II)	323.5	79

Future prospective

Many research efforts have been devoted to developing efficient materials as adsorbents with suitable, physical properties, microstructures, chemical compositions and surface functionalities for the removal of both organic and inorganic contaminants from aqueous media. The prospects of Sp-based materials as sorbent in water treatment are promising, because of its endowed natural properties. The highly cross-linked polymer Sp is extraordinarily stable, both chemically and physically. It was found chemically intact in 500 million years old sedimentary rocks [80]. This shows that Sp-based materials can withstand extreme conditions, thus making Sp a suitable solid support for grafting materials with surface functionalities that have high sorption affinity for target pollutants. It can form hybrids with other material by physically incorporating materials into the Sp's microcapsules pores [81] and chemical grafting through the functional groups (OH, COOH, CO) on the Sp [72]. Furthermore, Sp is environmentally friendly, readily available and biocompatible [80]. Therefore, Sp-based materials can serve as sustainable sorbents in water treatment of heavy metals.

Conclusion

Different Sp-based materials have been successfully synthesized and the ability of these Sp-based materials for removal of metal ions depends on their chemical nature, and various physicochemical properties such as adsorbent dosage, temperature, solution pH, adsorbent dosage. To enhance the ability of these Sp-based materials to remove metal ions, more research is needed on materials with high affinity for metal ions that can be grafted onto Sp. Among the reported Sp-based materials, GO@SiO₂-MSP@SiO₂NH₂ showed the highest adsorption capacity with Pb(II) $q_{\max}$ of 323.5 mmol/g, followed by CEP-Sp with 133 mmol/g for Cr(III).

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