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REVIEW

Removal and Recovery Through Chelate Ligand Modified Nanoparticles – A Case for Thiosemicarbazones

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Abstract

In the last decades, wastewater has developed from a burden to an essential part of water, energy, and nutrient supply. The curing of wastewater, especially the removal of toxic metal ions is thus important, and several technologies are currently employed. Amongst these technologies, adsorption is promising and the design of efficient and selective adsorbents is an important research area. The combination of high adsorption capacities with high selectivity might become feasible through anchoring of chelate ligands onto nanoparticles (NPs). Here, the typical NP characteristics as high surface areas, biocompatibility, and simple removability, were combined with specific properties of chelate ligands such as denticity and hard/soft donor sets allowing selective metal ion binding. Thiosemicarbazones (TSCs) with their general formula RR'C–N = N–C(S)–NR''R''' are attractive chelate ligands for the recovery of soft metal ions because they contain an N^S chelate binding pocket and the ease of modifying TSCs at the four position for substitution (R to R''') allows to even increase the number of donor atoms. Additionally, the same four positions can be used for functionalization towards covalent anchoring (conjugation) on NPs. In the first part of the review, in Chapters 1 to 4, general aspects of covalent binding (conjugating) of Ligands on NPs for metal recovery and removal is presented works. Chapter 5 then focusses on the idea of conjugating TSCs on NPs and presents recent progress in this field. Finally, some ideas are presented to further develop the field of TSC-modified NP for metal recovery and removal in Chapter 6.

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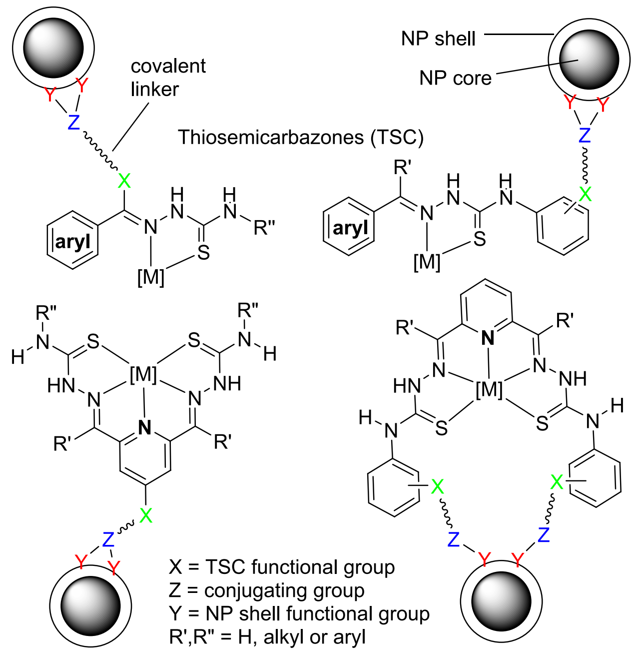
Graphical Abstract



Keywords Thiosemicarbazones · Chelate ligands · Nanoparticles · Covalent conjugation · Adsorption · Metals · Wastewater

1 Introduction

1.1 General Aspects

Human industrial, commercial, and infrastructural activities as well as daily life consumables include metal-containing materials have led to the generation of billions of tons of wastewater per day containing metal ions of concern such as Al^{3+}, AsO_4^{3-}, CrO_4^{2-}, Fe^{3+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, and Sn^{2+} [1]. Detecting, removing and recovering these toxic metal ions from wastewater is vital from a global health perspective [2–5]. Various methods have been developed to remove toxic metals such as chemical precipitation (including coagulation and flocculation), adsorption, electrochemical reduction, removal through membrane processes, reverse osmosis, and ion exchange methods [4–7]. Important goals are reducing the costs, simplifying the methods, avoid double contamination, and increase selectivity [2, 3, 7–9]. Amongst these methods, adsorption (chemi- and physisorption) is the most interesting in terms of sensitivity and selectivity [2, 3, 7–13] on which we will exclusively focus in this review.

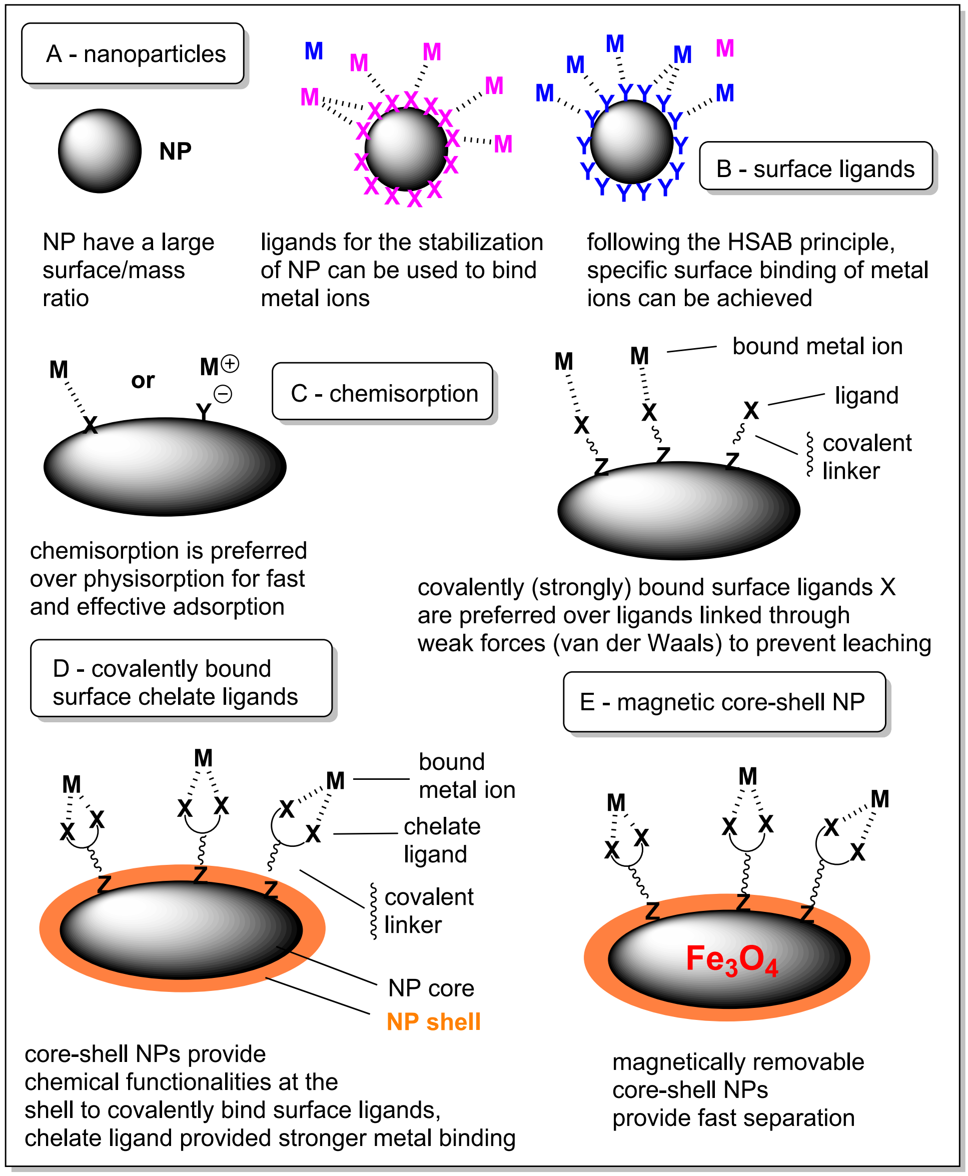
1.2 Functionalized Nanoparticles as Adsorbents

From the chemical engineering viewpoint, the main challenges in the removal of toxic metal ions from wastewater through adsorption are efficiency, separability, and recyclability of the adsorbent materials [2, 3, 14]. The following approaches separately or in combination have turned out to be beneficial. i) The choice of nanomaterials, especially nanoparticles (NPs) as adsorbent material; ii) The proper choice of surface functionalities (ligands); iii) Chemisorption instead of physisorption; iv) Chelate ligands bound covalently on the NP surface; v) magnetically separable core–shell NPs (Scheme 1).

In this review, we will focus on materials which follow the first four aspects. Thus, we will present concepts and modern approaches for the covalent binding (conjugation) of carefully designed or selected chelate ligands on NPs for chemisorption. The fifth aspect, the magnetic separability has turned out to be beneficial for the separation but is not essential for adsorption efficiency or selectivity.

Important for the adsorption process are the functional groups on the surface of the adsorbent material (Scheme 1B and C). They define whether the individual interactions are strong, which is the case when coordinative or ionic forces are used, or if the adsorption relies on the combined strength of several weak interactions such as hydrogen bonding, dipolar, or van der Waals interactions.

Selectivity of ligands for binding specific metal ions can be described based on the concept of hard and soft acids and bases (HSAB principle) [15]. Ligands characterized as hard bases contain small, highly negatively charged donor



Scheme 1 The benefits of covalently functionalized core–shell NPs as adsorbents for metal ions

atoms. They are strongly binding to hard metal ions which are characterized as being small and having high positive charges [16, 17]. In contrast, soft ligands containing large donor atoms with low charges bind preferably to soft metals which are characterized by large ionic radii and low charges. The proper application of the HSAB principle allows also discriminating between benign metal ions such as K^+, Na^+, Mg^{2+}, and Ca^{2+} which are all hard from toxic, soft, and heavy metal ions such as Pb^{2+}, Hg^{2+}, Cd^{2+}, and Sn^{2+} but also from soft, non-heavy metal ions of concern such as Cu^{2+} or Ni^{2+} (Scheme 1B).

Chelate ligands, also called chelators, provide more than one donor atom per ligand molecule. Such chelates can markedly increase the binding of metal ions compared to monodentate ligands through the so-called chelate effect [18–20], which also includes increased selectivity. Ethylenediaminetetraacetate ($EDTA^{4-}$) is a popular hexadentate ligand and has been used extensively in the design of selective metal ion adsorbents [21]. In a number of reports, EDTA has been covalently anchored onto Fe_3O_4 for selective binding of Cd^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+}, Fe^{2+} and Ni^{2+} ions [22, 23], onto SiO_2 for the removal of Zn^{2+}, Cu^{2+}, and Ni^{2+} ions [24], on graphene oxide (GO) for the removal of Pb^{2+} ions [25], and on metal–organic-frameworks for the removal of Eu^{3+}, Hg^{2+}, and Pb^{2+} ions [26–30]. Selectivity comes from its high negative charge ($EDTA^{4-}$) in the deprotonated state, preferring binding to trivalent over divalent metal ions, while monovalent ions are poorly bound. Some chelate ligands are also characterized by typical UV–vis, or IR absorptions and can thus easily be traced [31–33]. In general, magnetically separable adsorbent materials are preferable for easy processability [23, 31, 34–36].

2 Conventional Adsorbent Surfaces

There are many types of nanoparticular adsorbents employed in wastewater treatment. They include metal oxides [37, 38], clay [39, 40], carbon-based materials [41, 42], including those from natural resources such as chitosan, glucose, alginate, or biochar [43–47], as well as organic polymers [48, 49]. The adsorption capacity of an adsorbent depends on the surface properties such as texture, functional groups and charge. While for man-made polymers the chemical structure is clear and therefore the capacities to bind to metal ions are predictable from the functional groups of the polymers. For naturally occurring or derived materials, this is far less clear. And although such materials might be cheap and readily available, they do not have a defined chemical composition and thus their adsorption capacities are not reliable. The same is true for naturally occurring clay materials. In contrast to this, synthetic layered (clay-like) or porous materials such as amberlite, montmorillonite, and bentonite [50], represent defined structures and have been successfully used for the adsorption of metal ions [51, 52].

Metal oxides are the workhorses in the field of nanoscaled materials for the adsorption of metal ions.

In the sense of a preferred hard base/ligand – hard acid/metal interaction (HSAB principle), metal oxides such as Al_2O_3, Fe_2O_3, ZnO, CaO, MgO, and TiO_2 are suitable for the removal of hard metal ions such as Mg^{2+}, Ca^{2+}, and Mn^{2+} from aqueous solutions [16, 53, 54]. The surface hydroxyl groups on these metal oxides are considered the crucial site in binding the metal ions [55, 56]. For such a simple system, the adsorption capacity increases with the number of surface-located OH^- functions (Fig. 1) [57, 58].

As hydroxy functionalities on surfaces are not helpful in removing soft metal ions such as Hg^{2+}, Pb^{2+}, or Cd^{2+} from an aqueous solution, OH^- (hard base) ligand has been replaced by softer ligands such as cyanido CN^- and hydrogensulfido SH^- [59–61].

3 Surface-Modified NP Adsorbents

The functional groups on the surface of NPs are crucial for the binding and removal of metal ions from an aqueous solution. Pristine metal oxides typically covered with hydroxyl (OH^-) groups, which is a hard base in the HSAB principle [15], are effective in binding hard acids metal ions, such as Ca^{2+} and Mg^{2}. The functionalization of ZnO with softer and polyfunctional materials such as polyvinyl alcohol for the removal of Cu^{2+} ions from an aqueous solution is a typical example how designed surface ligands can improve metal binding and removal. The hydroxy-functionalized ZnO NPs were more efficient in binding Cu^{2+} with an adsorption capacity of 162.48 mg/g [57], compared to the non-functionalized ZnO NPs with 10.95 mg/g [58]. The surface-functionalization of NP can be achieved either through noncovalent blending of chelate ligands with NPs [58–67] or by covalently binding functional groups of the NPs to functional groups on the chelate ligands [67–70]. The resulting covalent binding of the chelate ligand to the NP surface is also called conjugation and will be in the focus of this review. In the following we will briefly introduce methods and traits of noncovalent NP functionalization and then focus on conjugation.

3.1 Noncovalent Functionalization

For noncovalent functionalization of NPs, chelate ligands are introduced during preparation [62], or in post synthetic stages [63]. In post-synthetic procedures, NPs are dispersed in a solution containing the chelate ligand, resulting in the deposition of the chelate ligands on the surface of the NPs [57, 63]. Alternatively, the chelate ligands are introduced during the formation of NPs i.e. at the nucleation stage, eventually causing the ligands to be trapped in the NP surface due to face segregation processes [62]. This method can also be used for noncovalent functionalized with polymeric materials such as cyclodextrin [62], polyvinylpyrrolidone [64], or activated carbon [65]. Noncovalent functionalization of NPs also has an impact on physical properties such as crystallinity, morphology, surface

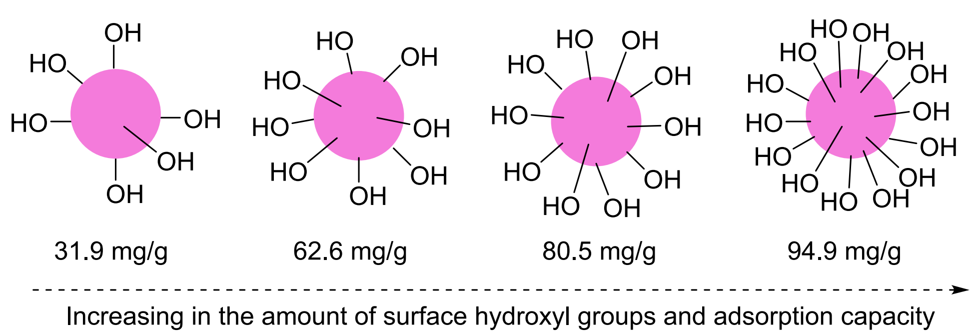


Fig. 1 Amount of surface hydroxyl groups on CeO_2 is increasing adsorption capacity. Adapted from Ref. [58]

area, and mesoporosity [66]. An example is the deposition of *N*,*N*-bis(salicylidene)−1,2-bis(2-aminophenylthio) ethane onto the surface of SiO_2 NPs for the detection and recovery of Pd^{2+} ions from an aqueous solution [66]. The functionalization resulted in an improved affinity of the functionalized SiO_2 NPs for Pd^{2+} compared to non-functionalized NPs, even at a reduced surface area and pore volume [66]. The advantage of noncovalent-functionalized NP adsorbent materials is their easy preparation. The disadvantage is the unclear binding of the ligands on the surface. The ligands might be partially engaged in binding to the NP surface, partially in binding the targeted metals. As a consequence, the ligand binding sites are not homogenous. If ligands are only loosely bound to the NP surfaces, disruption and leaking of metal complexes into the solution can be the result. All this would eventually reduce also the adsorption capacity.

3.2 Covalent Functionalization

Covalent functionalization, also called conjugation, is a more reliable approach as stable bonds between the NPs and the chelate ligand prevent leaching and allow selective binding of the metals at homogeneous ligand binding sites [67, 70]. Chelate ligands are anchored on NPs through chemical reactions between functional groups on both components [70]. The homogeneity of the ligand binding sites can be ensured by using a clearly defined functional group of the ligand for conjugation, which is not involved in metal binding. Techniques utilized in the covalent functionalization of NPs are discussed in detail in the next sections.

3.3 Examples for Surface-Functionalized NP Adsorbents

3.3.1 Silicon Oxide

The use of SiO_2 (silica) NPs as adsorbents for the removal of metal ions is essentially motivated by their commercial availability, or easy preparation, combined with established methods of surface functionalization, and last not least their low toxicity and biocompatibility [71, 72].

In an aqueous solution, the SiO_2 NP surface is hydroxylated and under basic conditions, the Si–OH surface function can be partially deprotonated yielding anionic Si–O⁻ surface groups. Both Si–OH and Si–O⁻ functionalities are very hard ligands (HSAB principle) and pristine SiO_2 NPs are suitable for adsorption of hard metals. For the adsorption of soft metals, SiO_2 NPs were frequently functionalized with amine, phosphate, thiol, or carboxylic acid functional groups [73, 74]. The chelate ligand-functionalized SiO_2 NPs can be obtained through reaction with functionalized alkoxysilanes such as 3-aminopropyltriethoxysilage (APTES) (Fig. 2) [75]. The new siloxane bonds are formed through the hydrolysis of the ethoxy silane groups, followed by a condensation reaction with surface Si–OH functions [75]. The simplicity of this method, the commercial availability of APTES and related silanes and the otherwise chemically quite inert surface of SiO_2 have made this method a standard for covalent functionalization of NPs [71, 72, 75–79]. Thiol-functionalized SiO_2 NP can be generated using 3-mercaptopropyl-trimethoxysilane [60], and phosphonic acids functionalized NPs using diethylphosphato ethyltriethoxysilane [18, 80].

The hydrolysis of (3-(2-aminoethylamino)propyl) trimethoxysilane and tetraethylorthosilicate (TEOS) in the presence of NH_4OH, afforded triamine-functionalized SiO_2 NPs used for the removal of Pb^{2+}, Cd^{2+}, Cr^{3+}, and Cu^{2+} ions in an aqueous solution [81]. TEOS serves to build-up

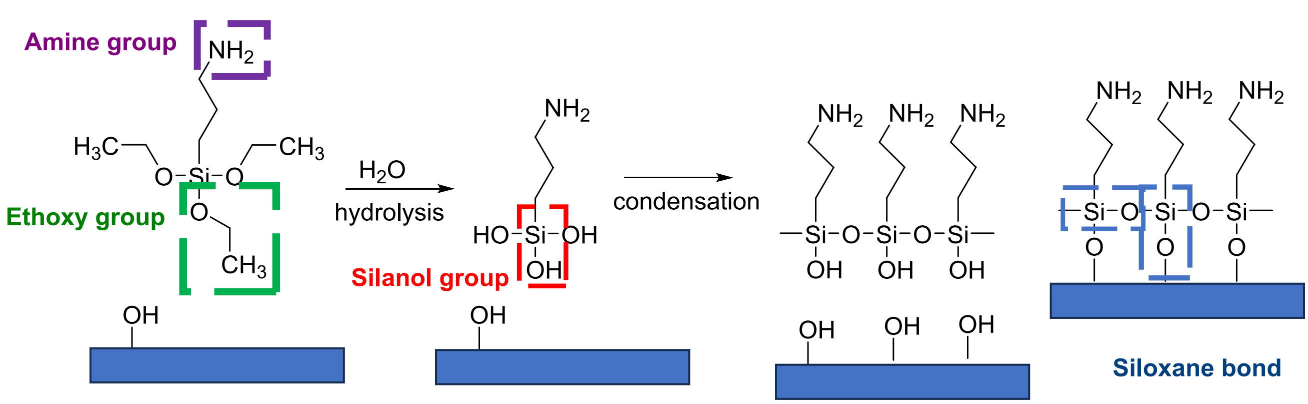


Fig. 2 Exchange of hydroxylated oxide surface with amino functional group, using (3-aminopropyl)triethoxysilane (APTES). The ethoxy and amine groups are the anchoring and functional groups, respectively. Adapted from Ref. [75]

the SiO_2 NP core, while the (3-(2-aminoethylamino) propyl)trimethoxysilane forms a shell allowing to covalently bind the chelate ligand. A further option SiO_2 NP functionalization is the use of propanoyl chloride [82].

Importantly, the covalent functionalization of NPs with chelate ligands also impacts the physical properties (pore size and volume) of SiO_2 NPs. E.g. The pore volume of the triamine-functionalized SiO_2 was found reduced from a value of 0.73 m^3/g for the pristine material to 0.14 m^3/g for the functionalized NPs [81, 83]. This is an indication that previously available hydroxyl sites (pores) have been clogged with amine-functional (-NH) groups, thus, bind more readily with hard metal ions.

Moreover, these functionalization techniques cannot only be used on SiO_2 NPs, but in the very same way also for core@shell NPs with SiO_2 shells [84–88]. A recent study showed clearly that the amount/concentration of anchored amine on the surface of Fe_3O_4 is the main contributing factor in removing metal ions such as Cu^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+} from an aqueous solution [88]. Increasing the amount of anchored amine on the surface of Fe_3O_4 between 0 to 15.12 mmol/g resulted in increased adsorption capacities (Fig. 3). Interestingly, the resulting SiO_2 shell and the deposited chelate ligand did not alter the magnetic properties of the amine-functionalized Fe_3O_4 [88].

Remarkably, the NPs core size was important parameter in a study on amine-functionalized Fe_3O_4@SiO_2 NPs for the removal of Cd^{2+}, Cu^{2+}, and Zn^{2+} ions from an aqueous solution [89]. The removal efficiency was a factor of the core size (103 nm > 123 nm > 207 nm). A lower core size obviously can translate to a higher specific surface area. The corresponding Brunauer–Emmett–Teller (BET) surface area was 483.78 m^2g^{-1}, 321.38 m^2g^{-1}, and 226.05 m^2g^{-1}, respectively. Thus, the amine-functionalized Fe_3O_4 NPs with the highest amount of reactive surface are beneficial in removing metal ions in an aqueous system because more $^{-}$NH functional groups are available on the surface of the Fe_3O_4 NPs for binding metal ions [87].

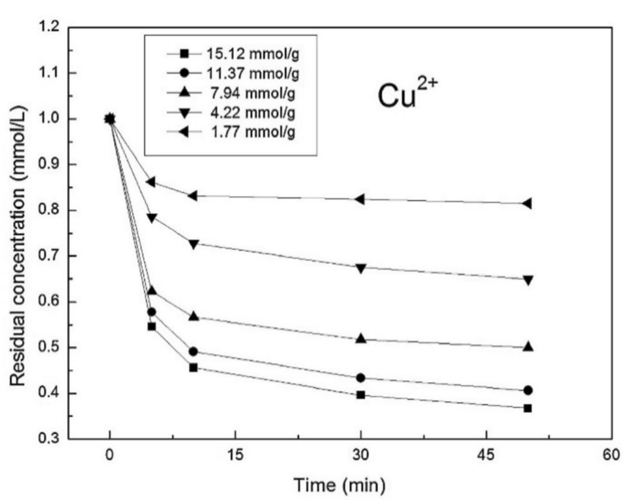


Fig. 3 Effect of increasing the degree of amination on the surface of Fe_3O_4 in recovering of metal ions. From Ref. [88], Lin S, Xu M, Zhang W, Hua X, Lin K (2017) J Hazard Mater 335:47–55. Courtesy by Elsevier, 2017

In the same way as iron oxides, other metal oxides can be used. E.g. thiol-functionalized Al_2O_3@SiO_2 NPs have been synthesized for the removal of Hg^{2+}, Pb^{2+} and Cd^{2+} ions from water, by treating alumina NPs with 3-mercaptopropyl trimethoxysilane in a solution of EtOH or toluene [60]. The adsorption rate constants of 0.0238 min^{-1}, 0.0222 min^{-1}, and 0.0169 min^{-1} for Hg^{2+}, Pb^{2+}, and Cd^{2+}, respectively showed the highest affinity of the thiol surface towards Hg^{2+} ions [60]. Thus, it is possible to selectively remove Hg^{2+} ions in the presence of Pb^{2+} and Cd^{2+} ions. The adsorption capacity of the alumina increased significantly from < 10 mg/g to 160 mg/g after functionalization with the thiol [60].

3.3.2 Aluminum Oxide

The high abundance, high stability, and low toxicity of Al_2O_3 is favorable for its technical use [90], which has led to several studies investigating the potential of Al_2O_3 NPs in removing metal ions from aqueous solutions [91–96]. Unfortunately, pristine Al_2O_3 NPs are poor adsorbents for removing metal ions from water. For instance, adsorption capacities of 9 mg/g and 14 mg/g for the removal of Cd^{2+} and Ag^{+} ions were reported for "nano-activated" Al_2O_3 [94]. For γ-Al_2O_3 NPs capacities of 6 mg/g, 1.1 mg/g, and 0.3 mg/g for the removal Pb^{2+}, Ni^{2+} and Cd^{2+} ions were reported [95]. In a very similar report, γ-Al_2O_3 showed capacities of 10 mg/g, 5 mg/g, and 5 mg/g for Pb^{2+}, Cd^{2+} and Zn^{2+}, respectively [96]. Therefore, Al_2O_3 NPs are usually modified to improve capacity and selectivity.

Thiol-functionalized Al_2O_3 nanofibers were used in the recovery of Pb^{2+} ions from aqueous solutions with removal efficiencies of the thiol-functionalized γ-Al_2O_3 NPs of up to 74% compared to 40% for the bare γ-Al_2O_3 NPs [97]. The adsorption efficiency was further enhanced to 95% by increasing the concentration of the thiol precursor during the adsorbent synthesis [97]. Al_2O_3-SiO_2 composite NPs were amine-functionalized using 3-aminopropyltriethoxysilane and 3-(2-amino-ethoxy) propylmethyldimethoxysilane for Cu^{2+} removal [98]. The surface-anchored branched chain 3-(2-amino-ethoxy) propylmethyl ligand seemingly had a strong impact on the specific surface area and allowed improving the adsorption capacity through increasing the silane precursor concentration during preparation (Fig. 4) [99]. Contrary to this, the Linear chain 3-aminopropyl ligand seems to have an impact on the pore size, but the adsorption capacity cannot be enhanced by increasing the precursors concentration [100].

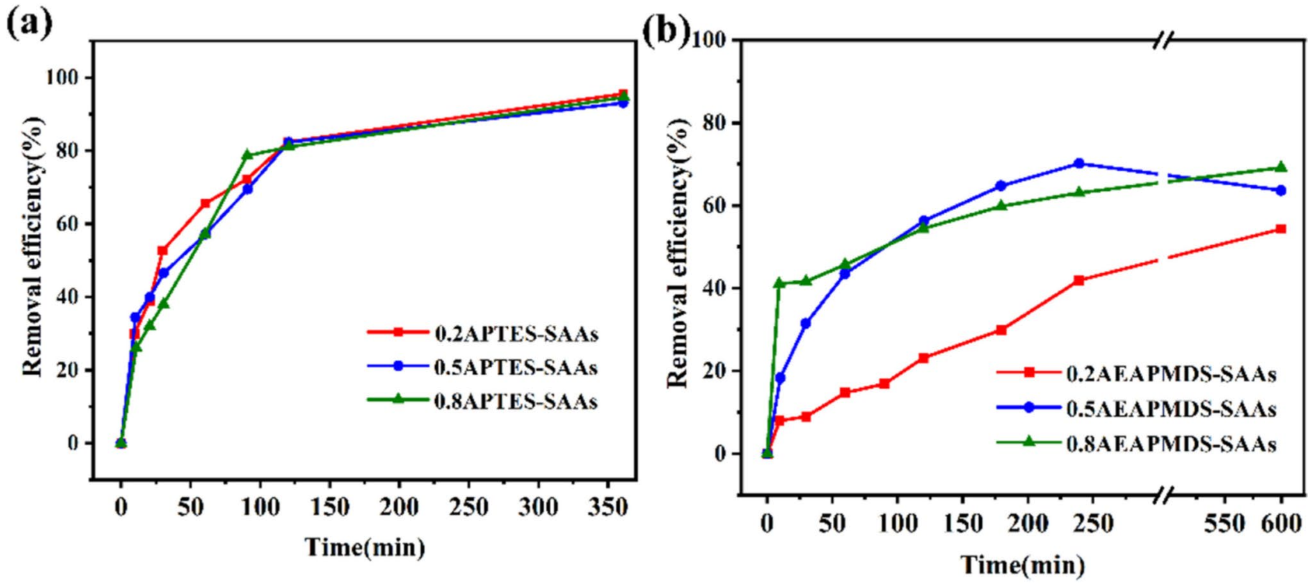


Fig. 4 Effect of chelate ligands modifiers NPS in removing Cu^{2+} ions from an aqueous solution. From Ref. [100], Yan F, Liu Y, Wang H, Zhang M, Guo M (2022) Environ Sci Pollut Res 2022:23655–23667. Courtesy by Springer, 2017

Mixed oxide Al_2O_3-SiO_2 NPs have also been functionalized with ligands bearing aldehyde and ketone functional groups for the removal of Cd^{2+} and Pb^{2+} ions from water [99]. The adsorbent was synthesized in a mixed solution of aluminum tri-*sec*-butylate, tetraethyl orthosilicate (TEOS), and 2,4-pentanedione as precipitating agent, followed by hydrolysis of 3-aminopropyl-trimethoxysilane in the presence of highly dispersed Al_2O_3-SiO_2 (Fig. 5). The

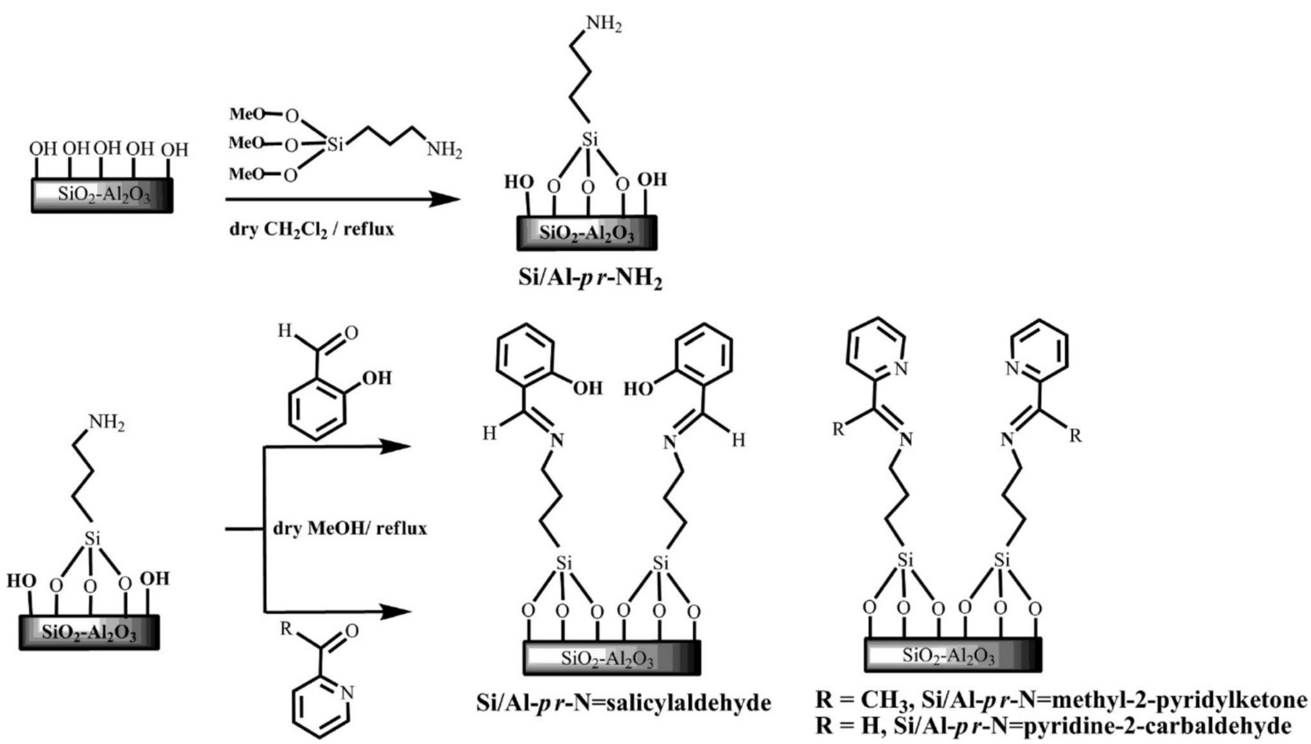


Fig. 5 Synthesis of Schiff base functionalized SiO_2-Al_2O_3 mixed oxide NPs for the removal of Cd^{2+} and Pb^{2+} ions from water. From Ref. [99], Arshadi M, Ghiaci M, Gil A (2011) Ind Eng Chem Res 50:13628–13635. Courtesy by American Chemical Society (ACS), 2011

BET surface area analysis of the Al_2O_3-SiO_2 material of 243 m^2/g is reduced after functionalization with salicylaldehyde 134 m^2/g, suggesting that the salicylaldimine ligand has blocked the surface of the Al_2O_3-SiO_2 NPs. The Al_2O_3-SiO_2 adsorbents could also function at extreme pH (1 to 2) with moderate efficiency [99]. This is an indication that functionalization with chelators with soft and hard base donor systems is beneficial in removing metal ions from an aqueous solution, even at extreme pH characteristic for wastewater.

So, there is a high similarity of functionalizing pure SiO_2 and mixed SiO_2-Al_2O_3 NPs which is due to the similar surface chemistry of SiO_2 and Al_2O_3.

3.3.3 Iron Oxides

Iron oxides (Fe_3O_4 and Fe_2O_3) are attractive materials due to their commercial availability or easy synthesis procedures combined with their magnetic properties, biocompatibility, and thermal stability [85–91]. Pristine iron oxides suffer from low adsorption capacity [53, 86]. Thus, functionalization with amine, carboxylic acids, phosphonic acid, and thiols, or with macromolecules is frequent [85, 86, 101–107].

Thiol-functionalized iron oxide NPs have been used extensively for the selective removal of mercury (Fig. 6) and precious metal ions from water [106]. For the same purpose humic acid/L-cystein-functionalized Fe_3O_4 NPs were used allowing high adsorption capacities over a large pH range [100]. This stands in contrast to a report on the removal of a series of metal ions, thiol-functionalized Fe_3O_4 NPs showed good capacities at near-neutral pH but poor adsorption at acidic pH. This is expectable, since the surface thiol functions are protonated at lower pH, while the binding strength of thiolate functions is far superior to thiols. The adsorption followed the series $Hg^{2+} > Pb^{2+} > Ag^{+} > Cu^{2+} > As^{3+} > Co^{2+} > Cd^{2+} > Tl^{+}$ [59].

The reason why the humic acid containing system is superior, lies probably in the excellent buffering properties of humic acid [100, 108].

4 Chelate Ligand-Functionalized Adsorbents

Chelate ligands can be classified following the number of the donor atoms [109]. Bidentate [108, 110–127], tridentate [82, 124, 128–136], tetradentate [134, 137–146], or polydentate [147–157] chelate ligands have previously been used in the functionalization of nanomaterials for the removal or recovery of metal ions from aqueous solutions (Table 1) [157–161]. At the same time, chelate ligands can be further classified through the arrangement of their donor atoms. For example, N^N^N^N [138] ligands, where the "^" in N^N, stands for the organic spacer connecting the two coordinating N ligand functions, were used for the removal of Pb^{2+}, Zn^{2+}, Ni^{2+}, Hg^{2+}, and Cd^{2+}, while an S^N^S^N ligand [122], was used for the removal of Zn^{2+}, Cu^{2+}, and Co^{2+}. Scheme 2 shows typical chelate ligand motives that have been used in selective metal binding [120, 123, 129, 139, 150, 152]. Although the superior ability of chelate ligands to bind metals can be assumed from the general idea of the "chelate effect", studies have explicitly shown that metal complexes formed from bidentate ligand functionalized adsorbents showed enhanced selectivity and adsorption compared with

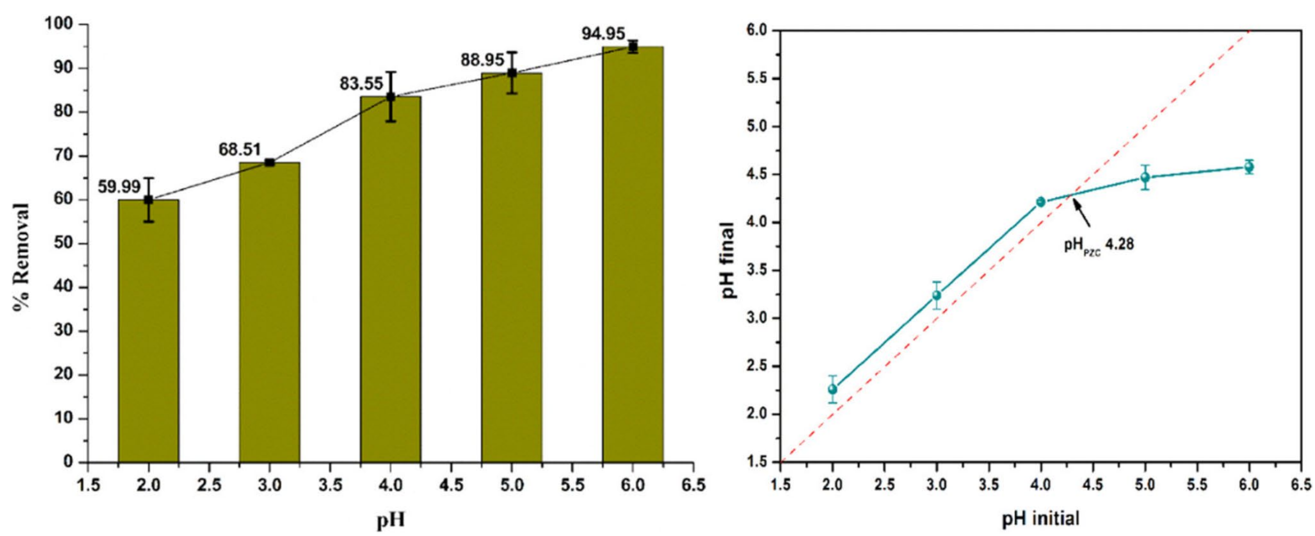
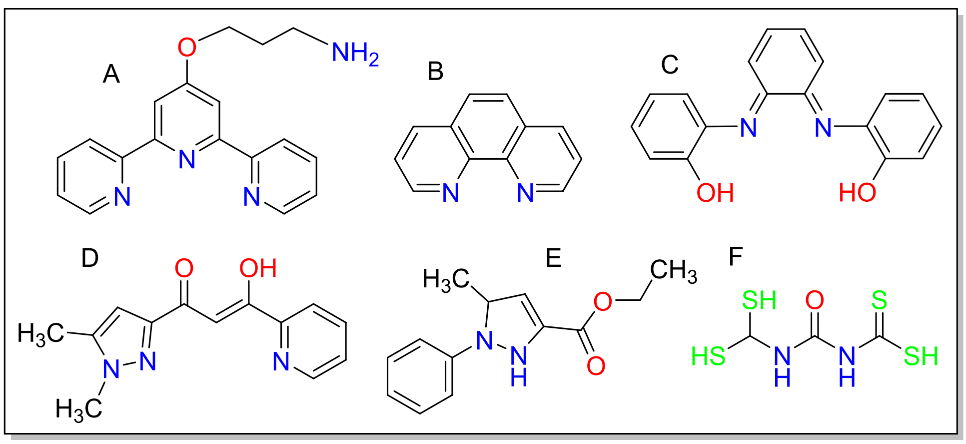


Fig. 6 Adsorption of Hg^{2+} ions at broad pH range attributed to the effects of multiply ligand system. From Ref. [100], Wan K, Wang G, Xue S, Xiao Y, Fan J, Li L, Miao Z (2021) ACS Omega 6:7941–7950. Courtesy by American Chemical Society (ACS), 2021

Table 1 Selected arrangements of donor atoms in ligand design for the removal of heavy metals

ligand type	metal ions	selectivity	Ref
O^S	Pb^{2+}, Cu^{2+}, Cd^{2+}	Pb^{2+}	[114]
N^S	Hg^{2+}, Zn^{2+}, Cd^{2+}, Al^{3+}, Fe^{3+}, Mg^{2+}, Ca^{2+}, Ag^{+}, K^{+}, Na^{+}	Hg^{2+}	[115]
N^S	Pb^{2+}, Cd^{2+}, Cu^{2+}	Pb^{2+}	[116]
CO^O	Cd^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}	Zn^{2+}	[117]
O^O	Pb^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+}	Pb^{2+}	[118]
N^N^S	Pb^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}	Ni^{2+}	[119]
S^S^S	Ag^{+}, Cd^{2+}, Hg^{2+}, Pb^{2+}	Hg^{2+}	[120]
N^S^S	Cd^{2+}, Cu^{2+}, Zn^{2+}	Cd^{2+}	[121]
N^N^N	Cu^{2+}, Pb^{2+}, Ni^{2+}	Cu^{2+}	[122]
O^S^O	Pb^{2+}, Zn^{2+}, Cd^{2+}	Zn^{2+}	[133]
O^P^O	Ca^{2+}, Mg^{2+}, Cd^{2+}, Ni^{2+}, Cu^{2+}, Pb^{2+}	Cu^{2+}	[138]
O^N^N^O	C^{u2+}, Pb^{2+}, Ca^{2+}, Al^{3+}, Co^{2+}, Au^{3+}, Fe^{2+}, Fe^{3+}, Ni^{2+}, Mn^{2+}, Zn^{2+}	Au^{3+}	[139]
N^N^N^N	Cu^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}	Cu^{2+}	[140]
O^N^N^O	Hg^{2+}, Ag^{+}, Na^{+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Mg^{2+}, Ba^{2+}, Pb^{2+}, Mn^{2+}, Ni^{2+}, Ca^{2+}, and Fe^{2+}	Hg^{2+}	[141]
O^N^N^O	Cu^{2+}, Na^{+}, Co^{2+}, Mg^{2+}, K^{+}, Ca^{2+}, Ni^{2+}, Zn^{2+}, Pb^{2+}, Mn^{2+}, Fe^{2+}, Al^{3+}	Cu^{2+}	[142]
CO^N^OC	Li^{+}, Na^{2+}, Mg^{2+}, K^{+}, Ca^{2+}, Zn^{2+}, Ag^{+}, Cd^{2+}, Hg^{2+}	Pb^{2+}	[143]



Scheme 2 Typical chelate ligands that has been employed for selective removal of metal ions from an aqueous solution. A = 4-(2,2',6',2″-terpyridin-4'-yloxy)butan-1-amine [129], B = 1,10-phenanthroline [123], C = 2,2'-cyclohexa-3,5-diene-bis-diphenol [139], D = (*Z*)−1-(1,5-dimethyl-1*H*-pyrazol-3-yl)−3-hydroxy-3-(pyridine-2-yl)prop-2-en-1-one [120], E = ethyl-5-methyl-1-pyridin-2-yl-1*H*-pyrazole-3-carboxylate [152]. F = dithiocarbamate [150]

metal complexes formed from monodentate functionalized adsorbents [121].

As discussed already above, the choice of donor ligands is usually made along the HSAB principle demanding that for the removal of soft metals (large, low charges) soft donor atoms such as P, S, Se, or N should be used, while hard metals (small, high charges) prefer hard donor atoms, O or N. For N atoms the type of functionality, such as amine, imine, or amide, aliphatic or aromatic, is decisive for a soft or hard character. For instance, the $N_{pyridine}$^N_{imine}^$S_{thiolate}$ binding 2-acetylpyridine-4-phenyl-TSC functionalized amberlite XAD-2 containing the very soft $S_{thiolate}$ function combined with the relatively soft $N_{pyridine}$ and N_{imine} functions, binds effectively to Pb^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Cd^{2+} [131].

Using thiol functionalized NPs, the soft Pt^{2+} and Pd^{2+} ions were selectively adsorbed in the presence of the "harder" Ni^{2+}, Cu^{2+}, and Cd^{2+} ions [162]. Pyridylpyrazole [120] and pyrazole-thiophene [163] functionalized NPs also bind preferably to Pb^{2+} in the presence of Zn^{2+}, Cu^{2+}, and Cd^{2+}. Hexamethylene diisocyanate covalently functionalized graphene oxide (GO) has been reported for the selective removal of Pb^{2+} [164]. Thus, through HSAB-governed choice of ligand components, chelate-based ligand NP adsorbents can be fine-tuned for a specific toxic metal pollutant.

The application of chelate-based adsorbent can also be extended to detecting metal ions specifically in wastewater. Amidoxime-functionalized cellulose was recently used for the simultaneous removal and detection of Cu^{2+} ions in an aqueous solution [165, 166]. The adsorption capacity was 326.6 mg/g, while the complexation reaction between the Cu^{2+} ions and amidoxime Ligands caused a broad absorption peaking at 700 nm.

The following section will focus on the current state of chelate-functionalized nanomaterials used in the recovery of metal ions from aqueous solutions. The specific properties induced by the presence of chelate on NPs, such as adsorption capacity and sensing characteristics will be discussed in some detail.

4.1 Adsorption Capacity

The adsorption capacity is the amount of adsorbate taken up by an adsorbent material per unit mass (or volume) of the adsorbent [167, 168]. It is one of the most essential parameters used in measuring the performance of an adsorbent. Chelate-functionalized adsorbents are characterized by high adsorption capacity (Table 2).

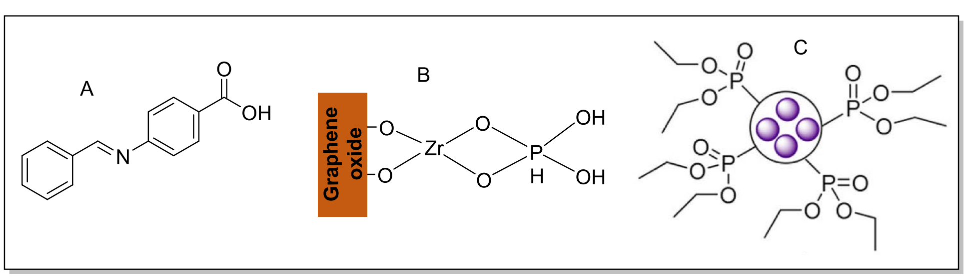
The enhanced adsorption capacity exhibited by chelate-functionalized adsorbents has been attributed mainly to the inherent donor atoms. The functionalization impacts the specific surface area, pore size, pore volume and diameter. The contribution of the phosphate ligand (P–O–H) in the removal of Cd^{2+} was examined using XPS analysis [118, 174]. The environment of the oxygen atom in P–O–H ligand was altered after adsorption. The intensity of the P–O–H peak reduced with the appearance of a new intense peak, corresponding to P–O–Cd [118, 174].

Increasing the number of donor atoms in chelate-functionalized NPs has also been an effective method to improve adsorption capacity. The adsorption capacity when a single donor atom was utilized for the recovery of Cu^{2+} ions in an aqueous solution was 34.08 mg/g [166], doubling the donor atoms resulted in an adsorption capacity of 328.56 mg/g [118, 166]. The high adsorption capacity of phosphonic acid-functionalized Fe_3O_4 NPs towards uranium ions was attributed to the presence of vinyl–O–P = O functional groups, which can form chelates with the uranium ions (Scheme 3) [118, 175, 176]. The composite Fe_3O_4/P(MMA-AA-DVP) was fabricated by polymerizing methyl methacrylate (MMA), acrylic acid (AA) and diethyl vinylphosphonate (DVP) in the presence of Fe_3O_4. The maximum adsorption capacity at room temperature was 413.2 mg/g at an initial pH of 4.5 [175]. Phosphonic acid-functionalized NPs also displayed a high adsorption capacity in removing $Th(OH)_2^{2+}$ ions in acidic wastewater [176]. The adsorption capacity corresponded to the amount of phosphonic acid functional groups on the adsorbent, which is in line with a strong coordination of $Th(OH)_2^{2+}$ ions to phosphonic acid. The adsorption capacity almost doubled from 243.3 mg/g to 403.2 mg/g, when the phosphonic acid content increased from 7.8% to 19.7% [176].

Table 2 Performance of ligand-functionalized SiO_2-based adsorbents

adsorbent material[a]	adsorbate	initial conc (ppm)	conditions pH	time (min)	dosage (mg)	adsorption capacity (mg/g)	Ref
MSN/*N,N'*-di(3-carboxysalicyclidene)−3,4-diamino-5-hydroxypyrazole	Co^{2+}	75.1	9.5	120	10	157.73	[169]
MSN/8-hydroxyquinoline	V^{2+}	50	4.0	5	100	492.61	[170]
MSN/*N,N*(octane-1,8-diylidene)di(2-hydroxy-3,5-dimethylaniline)	Pd^{2+}	72.1	1.5	180	10	213.67	[171]
silane-phosphonate[b]	Cr^{3+}	200	3.6	400	200	82	[172]
polysiloxane 4-acylpyrazolone	Yb^{3+}	6.7	6.7	1440	70	99%	[173]

[a]MSN = mesoporous silica nanoparticles [b]co-condensed oligomers of tetraethoxysilane (TEOS) and trimethoxysilylpropyl diethylphosphonate (DEPPS)



Scheme 3 Structural depictions of 4-{[(*E*)-phenylmethylidene] amino}benzoic acid (**A**) Zr-phosphate binding to the GO surface (**B**), and phosphonated Fe_3O_4/P(AA-MMA-DVP) NPs (**C**) for the removal of uranium ions. Adapted from Refs. [118, 175]

4.2 Signal and Detection

Chelate ligands covalently anchored on NPs form stable adsorbent materials, exhibit high adsorption capacity, and are selective towards the targeted metal ions in an aqueous solution, as we have discussed so far. In addition to this, the ligand might contain chromophoric moieties that can potentially be detected as markers through absorption or photoluminescence [161, 169, 177–185].

8-hydroxyquinoline-functionalized mesoporous silica nanoparticles (MSNs) were employed for V^{2+} adsorption and detection in wastewater through UV–vis absorption [170]. In addition to high adsorption capacity, the composite reliably detected V^{2+} in aqueous solutions in pH range from 2 to 12, even in trace amounts (~0.15 µg/L) [170]. Similarly, the *N,N'*-di(3-carboxysalicyclidene)−3,4-diamino-5-hydroxypyrazole ligand was attached to MSNs, for the removal and detection of Co^{2+} ions [169]. The ligand binds Co^{2+} yielding complexes with a characteristic absorption signal at 560 nm, allowing photometric quantification of Co^{2+}. However, the detection is strongly pH-dependent [169]. A similar strong pH-dependence was observed for the 2-hydroxyacetophenone-4*N*-pyrrolidine thiosemicarbazone (HAPT) supported on mesoporous SiO_2 for Hg^{2+} capturing from aqueous solutions, with the optimum pH lying at 12.5 [115]. In contrast to this, an *N,N*-(octane-1,8-diylidene) di(2-hydroxy-3,5-dimethylaniline)-functionalized MSN was reported to form a stable complex with Pd^{2+} at pH 1.5, resulting in color changes in solution from yellowish to blackish [171]. The presence of competing ions such as Ag^{+}, Cd^{2+}, Co^{2+}, Zn^{2+}, Fe^{3+}, Hg^{2+}, Cu^{2+}, Mg^{2+}, Ni^{2+}, Ca^{2+}, Ru^{3+} and Pt^{2+}, on the generated signal was negligible because, at the optimum pH, the interfering ions did not form a stable complex with the chelate [171].

In contrast to the absorbance increasing with the amount of metal ion coordinated to a ligand, ligand-based photoluminescence can be quenched by the presence of metal ions. As an example, 2,2,6,6-tetramethyl-1-piperidinyloxy was immobilized on cellulose for the detection of Cu^{2+} and Cs^{2+}. The luminescence intensity of the Cu^{2+} and Cs^{2+} decreased with increasing initial concentrations of Cu^{2+} and Cs^{2+} [182].

4.3 Chelate Ligand-Functionalized Adsorbents – Shortcomings

The adsorption capacity of ligand-based adsorbents is typically pH-dependent [184]. The Lewis basic donor atoms of a ligand are basically also Brönsted bases and can be protonated. This is especially true for the anionic and very basic thiolate, amide, and alcoholate functions of a ligand, which can easily be protonated and transferred to their thiol, amine, and alcohol forms, which are far poorer ligand moieties. The same is true for the neutral forms. E.g. protonation of an amine, which is a good ligand, to ammonium deletes its coordinative properties. At the same time, extreme pH values can hydrolyze the covalent conjugation between ligand and NP or change the surface "chemistry" of the NP. Both very high and very low pH values can lead to cleavage of polar conjugating units such as ester or amides. As an example, the complexation capabilities of phosphonate-functionalized-Fe_3O_4 NPs in removing uranyl were found acceptable only in a narrow pH range from 4.5 to 7.5 (Fig. 7). The failure at low pH values is due to the protonation of the phosphonates, while at high pH the surface anchoring of the phosphonates gets unstable [170].

Since adsorption is a surface phenomenon, the available specific surface area of the adsorbent is vital [180]. However, the process of anchoring chelate ligands onto NPs can result in the shrinking of important morphological parameters such as total surface, porosity, or pore size, thus reducing the capacity. An example is a report in which methyl-2-pyridylketone and pyridine-2-carbaldehyde were anchored on amine-functionalized SiO_2-Al_2O_3 aerogel NPs for the removal of Cd^{2+} and Pb^{2+} ions [99]. Prior to functionalization of the SiO_2-Al_2O_3 aerogels, the specific surface area, pore volume and pore size were 243 m^2/g, 0.028 cm^3/g and 20 Å, respectively. The initial NH_2-functionalization caused the specific surface area and pore volume to shrink by more than half. Further grafting of methyl-2-pyridylketone and pyridine-2-carbaldehyde, promoted the textural properties slightly with final values of 134 m^2/g, 0.018 cm^3/g, and 18 Å [99]. In a similar case, the N_2 adsorption/desorption isotherm of MSNs showed reduced BET surface (SBET), pore volume (Vp),

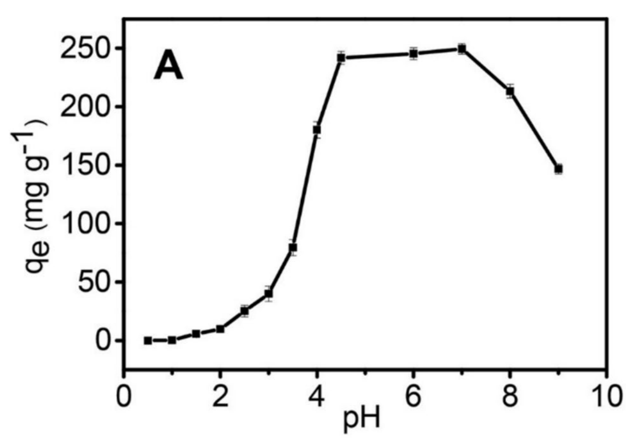


Fig. 7 Adsorption capacity (q_e) over pH. At pH < 2, q_e was negligible, while q_e was optimal between pH 4.5 to 7.5. From Ref. [175], Yuan D, Zhang S, Xiang Z, Liu Y, Wang Y, Zhou X, He Y, Huang W, Zhang Q (2018) ACS Sustain Chem Eng 6:9619–9627. Courtesy by American Chemical Society (ACS), 2018

and NP diameter (D) after functionalization with 5-*tert*-butyl-2-hydroxybenzaldehyde TSC (Fig. 9). The SEM confirms morphologic changes after the functionalization (Fig. 8, right) [186]. This shrinking phenomenon upon functionalization is frequently reported [115, 117, 169, 185, 187, 188].

Moreover, wastewater is a multicomplex solution containing different ions and molecules and even the proper choice of the ligand in terms of HSAB principle and denticity does not allow to specifically bind metal ions that are very similar in their chemical potential (size and charge). For example, amidoxime ligand-functionalized adsorbents are good candidates for the recovery and removal of uranyl from an aqueous solution, but the adsorbent capacity suffered in the presence of dissolved iron and vanadium [170, 189]. The competing ions formed stable complexes with the amidoxime-functionalized adsorbent causing a reduction in the adsorption capacity from 6.22 mg/g to 3.95 mg/g [189].

Nevertheless, the proper design of ligands and their efficient conjugation on NP surfaces remains the most promising approach to generate NP-based adsorbents with high capacities and selectivity. For both aspects, the large variation of ligand donor functions and the ease of covalent binding, makes thiosemicarbazones very interesting candidates as we will show in the following.

5 Thiosemicarbazones (TSCs) for Covalent Functionalization of Nanoparticle Adsorbents

5.1 TSCs as Ligands in Coordination Chemistry

Thiosemicarbazones (TSCs) are an interesting group of ligands. TSCs and their metal complexes have been studied intensely since the 1950s, mainly for their interesting biological properties but also for their rich coordination chemistry [70, 190–197]. TSC are formed from thiosemicarbazides and organic carbonyl compounds and show rich possibilities for substitution with up to four different groups (R to R''' in Scheme 4A). The general formula for a TSC reveals a thione-thiol tautomerism (Scheme 4B) [70, 147, 191, 197], and a five-ring chelate N^S binding pocket for the coordination to metals (Scheme 4C) with both thione and thiolate coordination having been reported [198, 199]. Many of the so far reported TSCs carry a heteroaryl group R. The frequently used 2-pyridyl group opens the possibility of the tridentate N_{Py}^N^S coordination with two five-ring chelates on the metal (Scheme 4D) [191, 192, 200, 201]. Bis-TSC ligands can be formed using di-carbonyl compounds (Scheme 4E) and allow for multidentate binding [147, 191, 193, 201–203].

TSCs as chelate ligands for the covalent binding to NP surfaces with the aim of adsorbing metal ions have several benefits. Although simple binding through the thiol group was reported in TSC complexes [191], the bidentate N^S binding using the thiol and imine functional groups is usually preferred [191, 192, 197, 201, 204, 205]. Additional binding functions can easily be introduced as substituents R to R'''

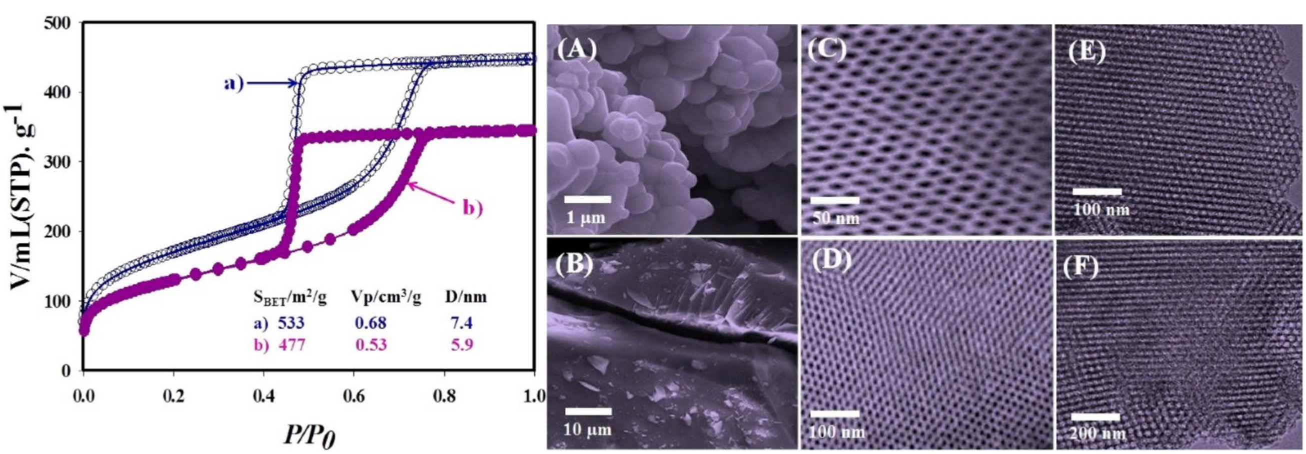
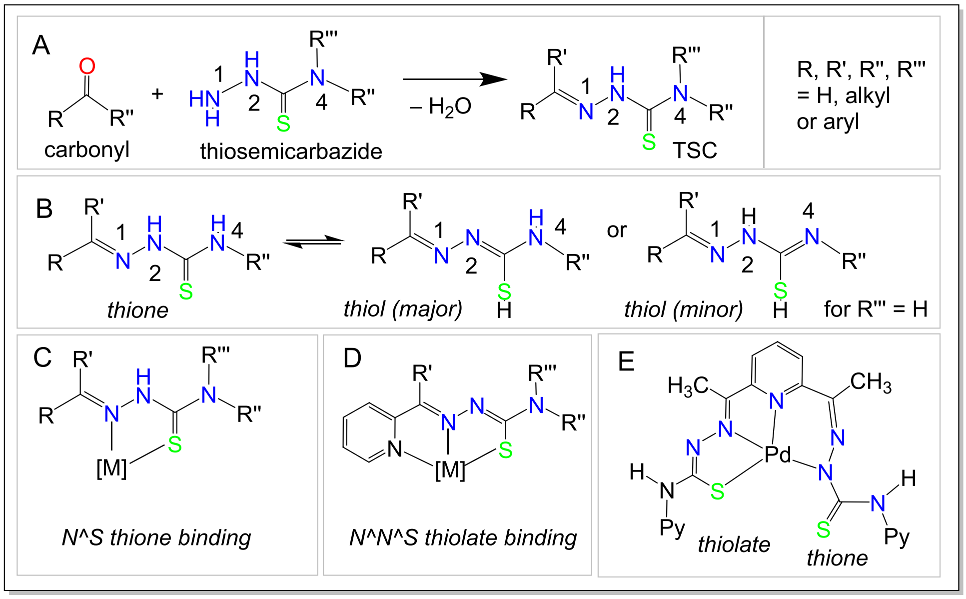


Fig. 8 Left: N_2 adsorption/desorption isotherms of (**a**) mesoporous silica monolith, and (**b**) TSC-functionalized adsorbent with BET surface (SBET), pore volume (Vp), and NP diameter (D). Right: SEM of mesoporous silica (**A**) and (**B**); STEM micrographs of uniform mesoporous silica (**C**) and (**D**) and TEM images after TSC-functionalization (**E**) and (**F**). From Ref [186], Awual MR (2015) A Novel Facial Composite Adsorbent for Enhanced Copper(II) Detection and Removal from Wastewater. Chem. Eng. J 266:368–375. Courtesy by Elsevier 2015

Scheme 4 **A** Formation of a thiosemicarbazone (TSC) from a thiosemicarbazone and a carbonyl. **B** TSCs in their thione and thiol forms (R, R', R'', R''' = H, alkyl, or aryl) with atom numbering. **C** N^S thione coordination of a TSC to metal fragments [M]. **D**: 2-acetylpyridine-thiosemicarbazones with potential tridentate N^N^S thiolate binding, **E** A potentially pentadentate 2,6-diacetyl pyridine bis-TSCs binding tetradentate to Pd(II) (from Ref. [147]



(Scheme 4C-E). Thus, multidentate TSC ligands can be generated [191–193, 196, 201, 206–209]. The introduction of further binding sites and general substitution of the TSC is facilitated by the modular build-up of thiosemicarbazides, TSCs, and bis-TSCs (Scheme 4) [70, 191, 201, 206–212].

The unsaturated character of the R'''R''N–C(=S)–NH–N=N–CRR' moiety, especially in the thiolate form R'''R''N–C(–S⁻)=N–N=N–CRR' is a reasonable chromophore [207], and potentially redox-active [201, 206, 212]. This is especially true for 2-pyridyl (Scheme 4D and E) and other heteroaromatic substituted TSCs [191, 193, 200, 201, 206, 209–211].

The most obvious suitability of TSCs for covalent anchoring on NPs comes from the up to four substituents R to R''' and very recently, we have reported on a number of functionalizations of TSC towards covalent anchoring on NPs or formation of conjugates to other molecules or materials [70].

In this review will present a step-by-step approximation to chelate ligand-functionalized NP to collect toxic metal ions from wastewater. We will start from simple surface-functionalized NPs and will discuss the choice of NP materials and their surface ligands, as well as their binding to the surface (surface modification). The relatively new field of chelate ligand-modified NPs will then be discussed. Finally, we will elaborate on the use of TSC as chelate ligands for chelate ligand-functionalized NPs.

A number of TSC ligands or TSC-containing polymers has previously been used for the detection or preconcentration of toxic or heavy metals [131, 179, 181, 193, 213–215]. Amongst them, 2-acetylpyridine-4-phenyl-3 TSC has been used for the recovery of Pt^{2+} in blood and urine samples [179], in petroleum oil and minerals [181]. The same ligand was also employed as a probe for the chemosensing of Ni^{2+}, Cu^{2+}, Co^{2+} and Cd^{2+} [213]. However, the use of TSC ligands for extraction of metals is quite limited as many TSCs are barely soluble in water and solvent mixtures must be used for such extraction procedures [179, 214, 215]. This makes TSC-functionalized materials for the removal of metals superior to unsupported TSC ligands in solution. We will therefore focus especially on TSC-functionalized nanomaterials (TSC conjugates) in the next Sect. (5.2).

5.2 TSC-NP Conjugates for Removal and Recovery of Metal Ions

The performance of reported TSC-based adsorbents showed that the binding of TSC-based adsorbents with metal ions is spontaneous, showing high adsorption capacity (Table 3). In a comparative study, the adsorption of Pb^{2+} ions on multiwall carbon nanotubes (MWCNs), carboxylate functionalized MWCNs, and 1-isatin-3-TSC-conjugated carboxylate-functionalized MWCNs was evaluated [216]. The adsorption capacity of carboxylate-functionalized MWCNs anchored with 1-isatin-3-TSC was superior (63.67 mg/g), when compared with the solely carboxylate-functionalized MWCNs (7.36 mg/g) up to a pH of about 5 which is in line with the soft Pb^{2+} ions preferring the "softer" TSC over the hard carboxylates [216]. In a further study, the modification of MSNs with a 2-hydroxyacetophenone-4-*N*–pyrrolidine-TSC ligand altered the textural properties of the resulting adsorbent [115]. The adsorbent was employed for the selective removal of Hg^{2+} in a basic aqueous solution. The adsorption capacity was and strongly depending on the pH and reached 172.61 mg/g at about 12.5 (Fig. 9). The

Table 3 Efficiency of TSC-functionalized adsorbents in removing metal ions from aqueous solution

adsorbent material[a]	adsorbate	initial concentration (mg/L)	time (min)	adsorbent dosage (mg)	optimum pH	adsorption capacity (mg/g)	Ref
MWCNT@isatin–TSC	Pb^{2+}	50	30	60	5.5	63.69	[216]
GO@2-PCA-TSC	Hg^{2+}	20	3	6	5	309	[217]
Al_2O_3@isatin TSC	Cr^{3+}	0.1 (M)	30	50	1	200 µmol/g	[220]
Al_2O_3@isatin TSC	$C_2O_7^{2-}$	0.1 (M)	30	50	7	780 µmol/g	[220]
MSN@5TBHB-TSC	Pd^{2+}	70.01	180	10	3.5	171.65	[188]
MSN@ACMPC	Pd^{2+}	80.14	180	10	2.0	157.23	[219]
MSN@5TBHB-TSC	Eu^{3+}	100.0	180	10	5.0	176.31	[218]
MSN@5TBHB-TSC	Cu^{2+}	2.0	12	8	7.01	176.27	[186]

[a]GO = graphene oxide, MWCNT = multi-walled carbon nanotubes, MSN = mesoporous silica nanoparticles, PCA = pyridine-carboxaldehyde, 5TBHB = 5-*tert*-butyl-2-hydroxybenzaldehyde, ACMPC = ammonium (4-chloro-2-mercaptophenyl)carbamodithioate

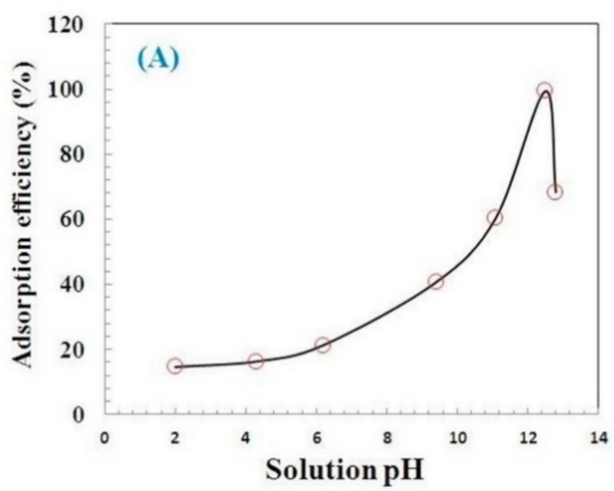


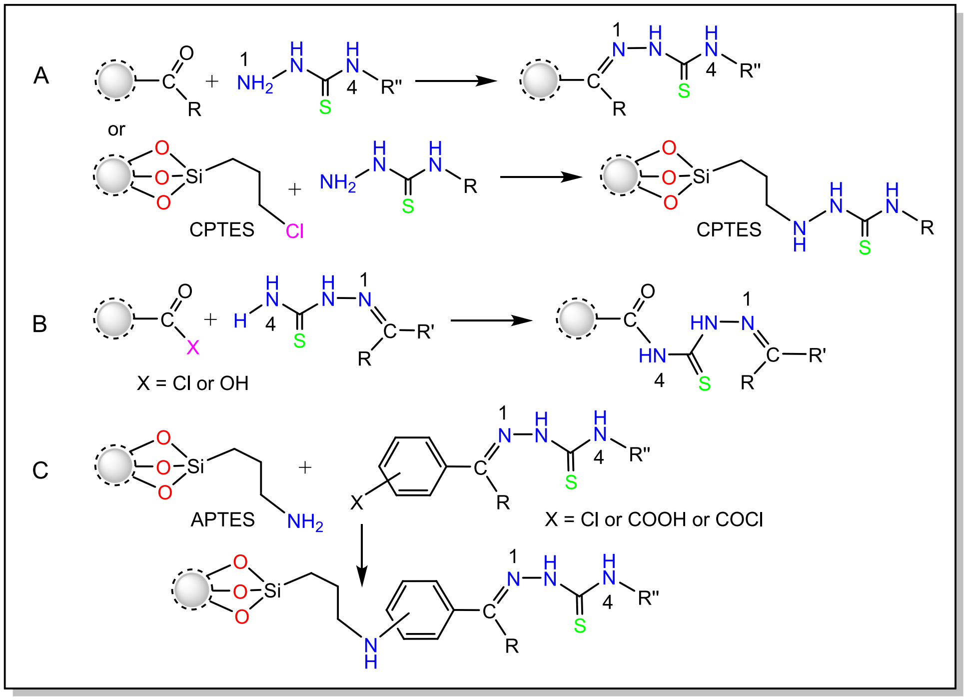
Fig. 9 The selectivity of Hg.$^{2+}$ in basic medium using MSNs functionalized with 2-hydroxyacetophenone-4-*N*–pyrrolidine TSC. From Ref. [115], Abbas K, Znad H, Awual MR (2018) Chem Eng J *334*:432–443. Courtesy by Elsevier, 2018

poor adsorption capacity at low pH was attributed to the protonation of the TSC surface ligands and the generation of $Hg(OH)^+$ and $Hg(OH)_2$, which culminated in a possible adsorbent-adsorbate repulsion.

A maximum capacity of 309 mg/g for Hg^{2+} ions was achieved when anchoring 2-pyridinecarboxaldehyde onto graphene oxide [217]. The improved affinity for Hg^{2+} is probably due to the presence of the 2-pyridyl group making up a $N_{pyridyl}$^N_{imine}^$S_{thiolate}$ coordination, very favorable for Hg^{2+} binding. MSNs were used as support to anchor 5-*tert*-butyl-2-hydroxybenzaldehyde TSC (5TBHB-TSC). The resulting MSN@5TBHB-TSC adsorbent was used for the removal of Pd^{2+} with a maximum capacity of 171.65 mg/g [188]. At the optimum pH of 3.5, in the presence of 10 mg/L competing ions (Ca^{2+}, Fe^{3+}, Co^{2+}, Mg^{2+}, Zn^{2+}, Cu^{2+}, K^+, Na^+, Ag^+, Ru^{3+}, Al^{3+}, Ba^{2+} and Pt^{2+}), the composite was selective for Pd^{2+} at 2 mg/L initial concentration, with slight loss of activities after the 9th cycle of the regeneration of the adsorbent [188]. The same adsorbent material was also used for the recovery of Eu^{3+} [218]. For the purpose of Pd^{2+} detection and recovery, alternatively (4-chloro-2-mercaptophenyl)carbamodithioate attached to MSNs has been reported [219], and recently, a potentially pentadentate bis-TSC Ligand based on 2,6-diacetyl-pyridine was conjugated to Fe_3O_4@SiO_2 core–shell nanoparticles for application in Pd^{2+} recovery [147]. The MSN@5TBHB-TSC adsorbent was also used for the detection and removal of Cu^{2+} from an aqueous solution. The removal of Cu^{2+} ions was strongly influenced by the solution pH and a maximum adsorption capacity of 176.27 mg/g was found at neutral pH [186].

A stable alumina-functionalized isatin-TSC was employed for the preconcentration and selective extraction of Cr(III) and Cr(IV) in the presence of competing metal ions [220]. The affinity of the adsorbent towards Cr^{3+} increased with increasing pH from 4 to 7, with adsorption capacities between 10 and 760 µmol/g. In contrast, the affinity for $C_2O_7^{2-}$ increased as the initial pH solution decreased from 4 to 1, with adsorption capacity ranging from 100 to 400 µmol/g. This different behavior is in keeping with the very different species Cr^{3+} vs. $Cr_2O_7^{2-}$ [221]. However, recently polyethyleneimine grafted onto $NiFe_2O_4$@SiO_2 core@shell NPs was used as adsorbent for CrO_4^{2-}, Ni^{2+}, and Pb^{2+} with adsorption capacities of 149.3, 156.7, and 161.3 mg/g, repsectively. For all three ions, the optimum pH was found around 6.8, which can only mean that not the anionic CrO_4^{2-}, but the reduced form Cr^{3+} was adsorbed [221]. Polystyrene NPs modified with 1-phenyl-1,2-propanedione-2-oxime-TSC were employed for the preconcentration of Cu^{2+} ions in aqueous solution, soil and food samples [222]. The TSC-functionalized polystyrene selectively bound Cu^{2+} at initial pH of 5. The adsorbed Cu^{2+} exhibits high stability in strong acid and alkaline mediums.

Scheme 5 Three approaches to generate NPs covalently functionalized with TSCs, note the numbering of the TSC N atoms



However, competing ions such as Fe^{3+} and Hg^{2+} remain a challenge [222].

Therefore, while TSC-based adsorbents show high adsorption capacity, and can function in selective extraction and preconcentration, competing ions remain a challenge. However, this shortcoming can be overcome by manipulating the initial pH of the solution, since both N and S donor atoms in TSCs can basically function independently at opposing pH values.

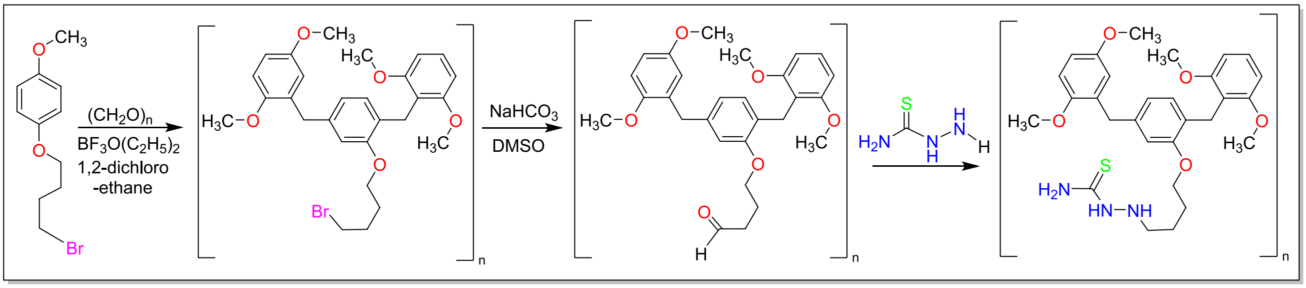
As the recovery of metal ions after adsorption onto adsorbent is important for a sustainable development and ecological concerns [1, 3, 6, 7, 223]. Therefore, not only the efficient adsorption but also the desorption of adsorbed metal ions is an essential factor in removing and recovery of metal ions from an aqueous solution. Typically, the desorption of metal ions from TSC-based adsorbents is achieved by contacting in dilute acids solution [224]. For instance, 97% desorption was achieved by washing a Cu^{2+}-laden TSC-based adsorbent in a 0.1 M HCl [225]. The use of a dilute acidic solution in the desorption of adsorbed metal ions from TSC-based adsorbents is highly feasible since TSCs exhibit basic properties, especially the S function is in most transition metal complexes is present as very basic thiolate [147, 191, 192, 198, 199, 201].

6 Perspectives on Covalent Functionalization of TSCs

In this last chapter, we will provide selected recent examples of TSC-NP conjugate adsorbent materials and their synthesis. These materials represent promising concepts for further developments in this field. There are basically three different approaches so far reported to covalently bind TSC ligands to the surface of a NP material (Scheme 5).

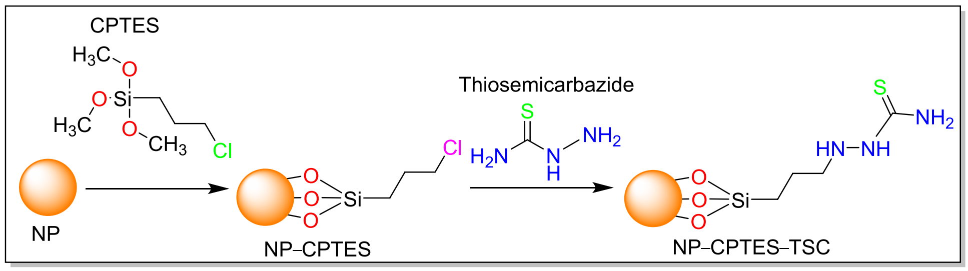
The simplest approach for the covalent anchoring of TSC on NPs is the reaction between the thiosemicarbazide hydrazine (N1) function and a carbonyl function bearing NP (Scheme 5A). The reaction of a carbonyl compound with the hydrazine function of a thiosemicarbazide is the conventional way to form TSCs (compare Scheme 4A). This method has been used for ribose, galactose and glucose [226–228], but has meanwhile being adapted for materials such as for the fabrication of a calixarene-type pillar[5]arene TSC (Scheme 6) [229].

Alternatively, SiO_2 NPs were functionalized with 3-(chloropropyl)trimethoxysilane (CPTES) providing them with a halogen end-group (compare Scheme 5A).



Scheme 6 Acylation of pillar[5]arene and condensation with thiosemicarbazide. Adopted from. Ref [229]

Scheme 7 Synthesis of SiO_2–TSC NP conjugates using CPTES-Cl. Adopted from Ref. [231]



Thiosemicarbazide hydrazine groups can react with this Cl function forming a SiO_2–CPTES–TSC conjugate. (Scheme 7) [230].

In a similar way, Fe_3O_4@SiO_2 core–shell NPs were pre-functionalized with 3-(chloropropyl)trimethoxysilane (CPTES) and 4-hydroxyacetophenone (HAT) to introduce an aldehyde group, followed by the reaction with thiosemicarbazide to afford Fe_3O_4@SiO_2–CPTES–HAT–TSC [232, 233]. Very recently, SiO_2 NPs were pre-functionalized with CPTES and reacted bis(2-aminoethyl)amine to form a SiO_2–CPTES–$N(CH_2CH_2NH_2)_2$ conjugate for the removal of Pb^{2+} from wastewater [231], while shows that this approach of using CPTES-Cl-functionalized SiO_2 NPs can be used for various amine-bearing ligands.

In an alternative approach, pre-functionalized NPs can be reacted with the TSC $N(4)H_2$ group (Scheme 5B). For the functionalization of graphene oxide (GO), the pending carboxylic acid groups of GO were transformed into carboxylic acid chlorides and reacted with the 2-pyridyl TSC $N(4)H_2$ (Fig. 10) [217]. For multi-walled carbon nanotubes (MWCNTs) the $N(4)H_2$ end-groups of the acenaphthenequinone bis-TSC was reacted with carboxylated MWCNTs [234]. The same method has been reported for the conjugate of the 1-isatin-3-TSC with MWNCTs for the removal of Pd^{2+} ions [216]. Recently, chitosan was stepwise functionalized using CS_2 and hydrazine to build-up a chitosan thiosemicarbazide, which was then reacted with salicylaldehydes [235].

TSC-functionalized CuO NPs (CuO@COOH–TSC) were synthesized by the pre-functionalization of CuO with glutamic acid, followed by condensation with the TSC $N(4)H_2$ moiety (Scheme 8) [236, 237]. Similarly, ZnO@COOH–TSC, Pt@COOH–TSC and TiO_2@COOH–TSC have also been synthesized for biomedical purposes [238–240]. Fe_3O_4 was pre-functionalized with biotin hydrazide to bear an aldehyde, the reaction with thiosemicarbazide afforded Fe_3O_4@Biotin–TSC for ^{68}Ga-labeling [241].

Chitosan pre-functionalized (coated) Fe_3O_4 NPs have been reacted with Pd(II) TSC complexes [242]. This would be a very elegant way to produce NP-TSC-complex conjugate, but in this example, the covalent bonding was not supported by direct experimental evidence. Instead, the authors report that after functionalization with the Pd(II) TSC complexes, the size of the NPs was reduced, which points to an uncontrolled re-organization of the particle surface. While such NP–metal complex conjugate materials are of interest for biomedical or catalytic applications [210, 241–249], this method is not interesting for metal recovery or removal. However, the idea to selectively extract metals from mixtures through carefully designed metal-selective ligands through cross-linking the initially formed metal complexes to the NP surface sound appalling (Scheme 9). While the recovery or removal of metals using auxiliary ligands is well-established [2, 4, 7, 8, 10, 249, 250], especially for uranyl separation [251], this "fishing-through-conjugation" approach needs to be developed. The terminal $N(4)H_2$ group of TSCs seems to be reactive enough to provide covalent conjugation to a pre-functionalized NP.

A third approach is the use of pre-functionalized TSC ligands (compare Scheme 5C). Very recently

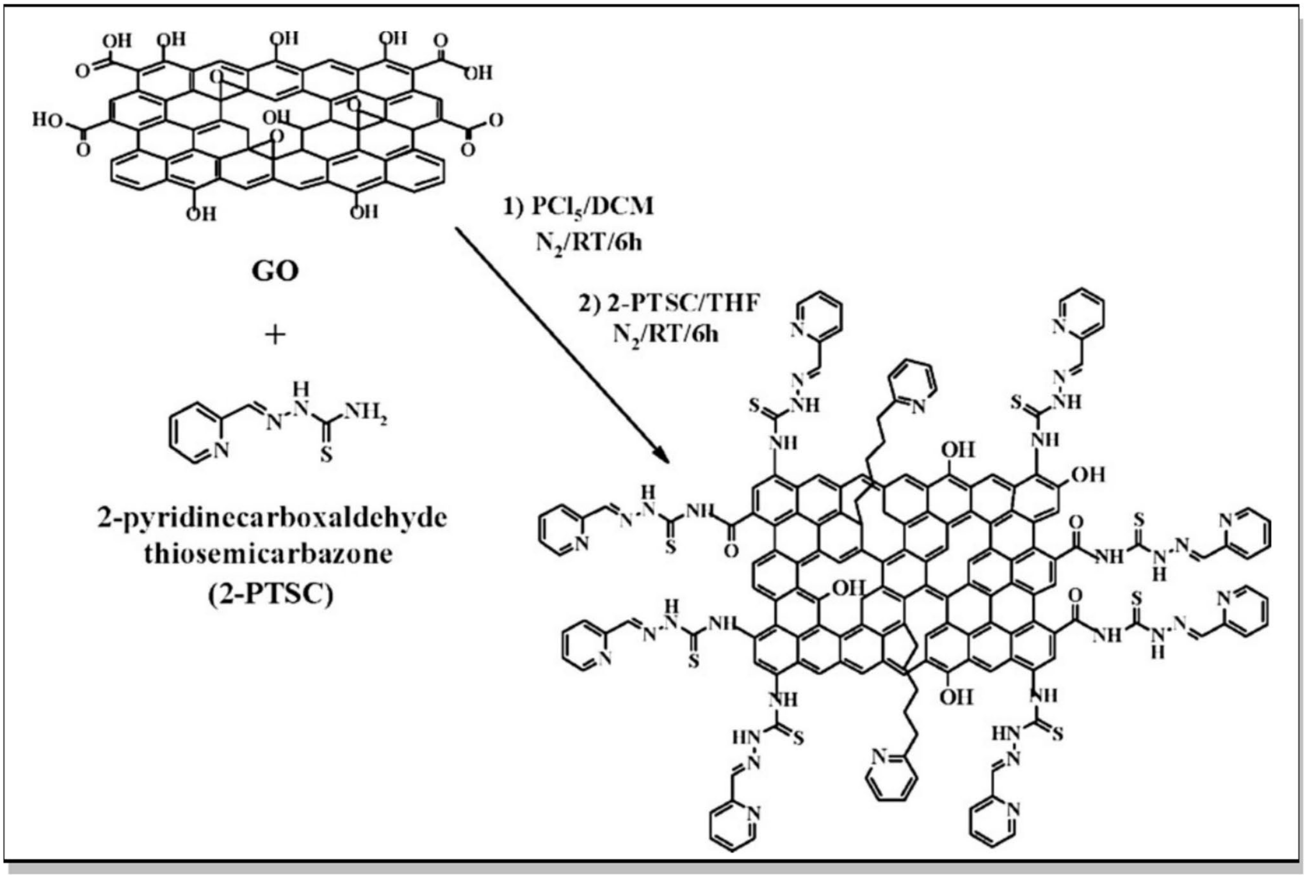
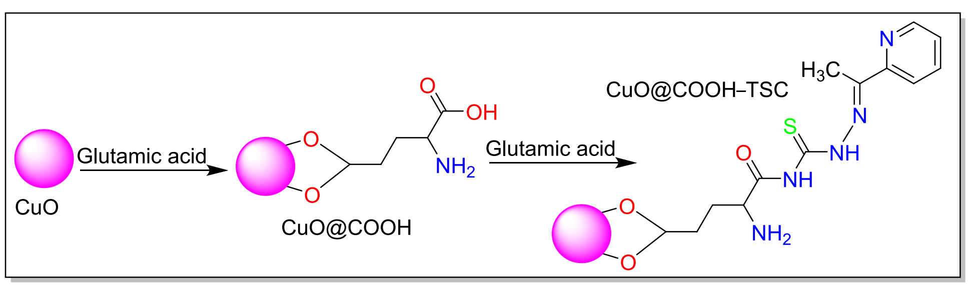


Fig. 10 Covalent anchoring of TSCs onto graphene oxide. From Ref. [217], Tadjarodi A, Ferdowsi SM, Zare-Dorabei R, Barzin A (2016) Ultrason Sonochem 33:118–128. Courtesy by Elsevier, 2016

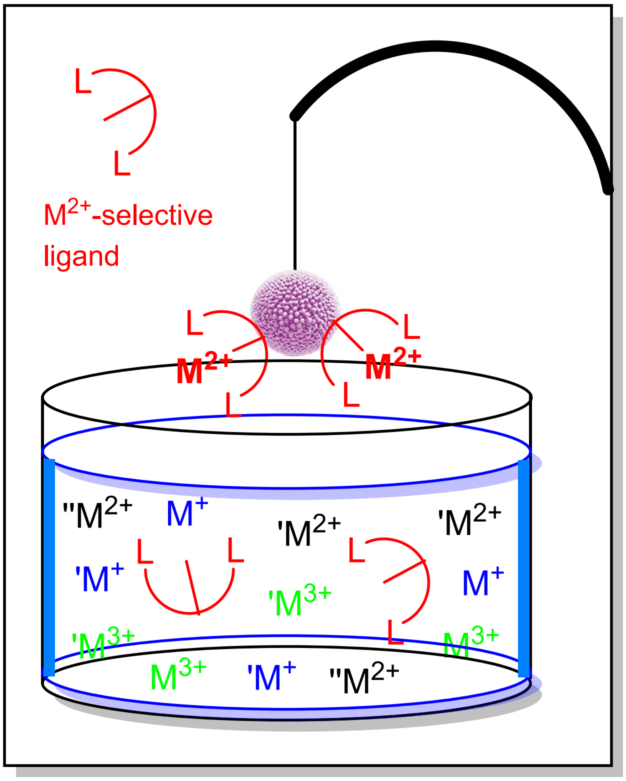
Scheme 8 Synthesis of TSC-functionalized CuO NPs. Adopted from Ref. [236]



a HOOC-functionalized bis-TSC Ligand based on 2,6-diacetyl-pyridine was reacted with core–shell $Fe_3O_4@SiO_2$–APTES NPs to form an amide conjugate (Scheme 10A) and used for the recovery of Pd(II) from aqueous solutions [147]. While the reaction of K_2PdCl_4 with the unfunctionalized ligand BTSC gave a $S_{thiolate}$^N_{imine}^$N_{pyridine}$^N_{amide} coordinated complex (Scheme 10B left), the X-ray photoelectron spectroscopy of the $Fe_3O_4@SiO_2$–APTES–BTSC NP adsorbent suggested a contribution from a chlorido-coordinated complex species with a tridentate $S_{thiolate}$^N_{imine}^$N_{pyridine}$ coordination of the TSC ligand (Scheme 10B, right). This underpins the coordinative flexibility of this potentially pentadentate bis-TSC ligand [147].

A very similar pentadentate Cl-substituted bis-TSC ligand was reacted with SiO_2–ATPTES NPs to give a very similar NP–TSC-ligand conjugate as that shown in Scheme 10. The conjugate was coordinated to Pd(II) and used as supported homogeneous catalyst for Suzuki–Miyaura-type C–C cross coupling reactions [252].

Basically, the functionalization of the TSC for the covalent connection of TSCs to the NPs, marked in green in Scheme 11, can be located at the R’ (**A**) or the R’’ (**B**)



Scheme 9 Selective "Fishing" for metal ions using covalent crosslinking (conjugation) NPs to metal-selective ligands (fishing-through-conjugation method)

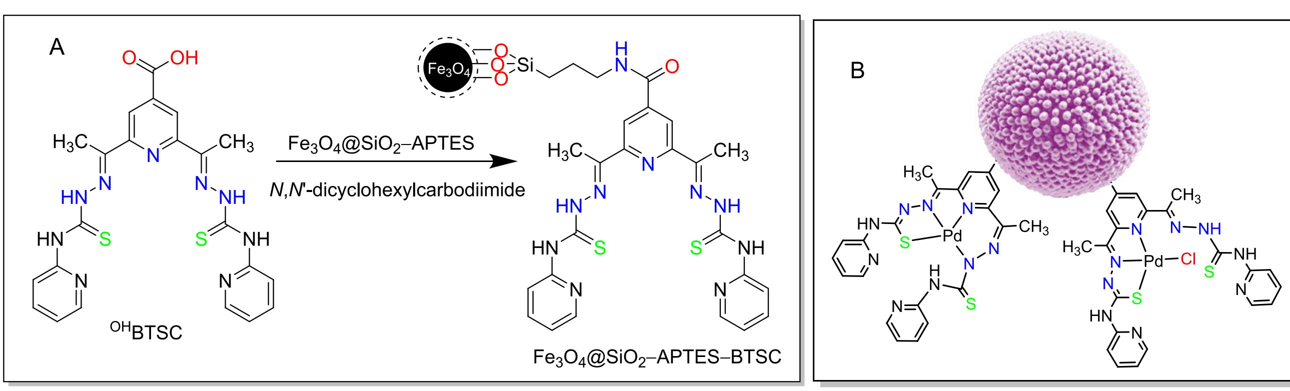
position. Bis-TSC ligands might thus be anchored at two positions, increasing their binding stability (Scheme 11C).

Very recently essential preliminary work on the functionalization of TSC on all possible positions has been worked out in detail [70], showing more promising approaches for using TSC as conjugating link between complexes, peptides and other biologically relevant molecules, and NPs.

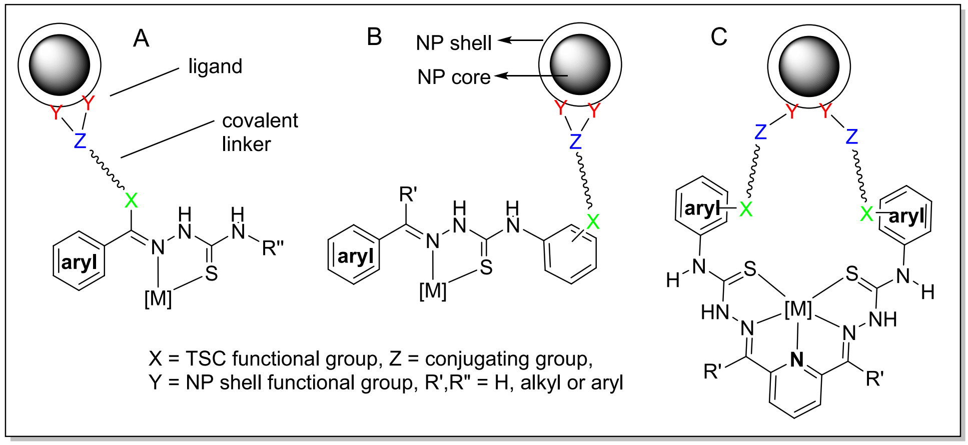
7 Conclusions

In this review we outlined the role of thiosemicarbazones (TSCs) as covalently bound (conjugated) ligands on nanoparticles (NPs) for the binding and removal of toxic metal ions from wastewater or related applications. TSCs with their general formula RR'C–N = N–C(S)–NR''R''' are primarily known for their biological properties, which are mainly due to their ability to form N_{imine}^$S_{thiolate}$ chelates with redox-active metal ions such as Fe(II), Fe(III), or (Cu(II) in vivo. Their formula also reveals that through proper substitution at the R to R''' positions, the coordinating properties of TSCs can be greatly extended with the introduction of additional coordinating functions. This includes also further donor atoms such as O, C, or P adopting binding preferences of specific metal ions following the HSAB principle. With such polydentate TSC ligands, selective metal coordination and removal is possible. Furthermore, the multiple substituents allow to covalently bind (conjugate) the TSCs on nanoparticle (NP) surfaces, thus creating the perfect adsorbent material for removal of toxic metal ions from wastewater or the recovery of precious metals.

TSC have previously been used for this purpose alongside a plethora of other polydentate ligands, but the modular synthesis of TSCs from carbonyls (RR'C = O) and thiosemicarbazones ($H_2NNC(S)NR''R'''$), that can be readily prepared from amines HNR''R''', make them superior to other ligand classes. Chemically, the TSC moiety is air and moisture stable and withstands also harsh acidic or basic conditions. Furthermore, the easy introduction of the R to R''' substituents allows to tailor-make the anchoring groups for the NP conjugation. TSC are superior to many other ligands as their multiple substituents allow conjugation at positions which are remote of the metal binding pockets including the



Scheme 10 **A** A HOOC-functionalized bis-TSC ligand is conjugated to $Fe_3O_4@SiO_2$–APTES NPs. **B** Model complexes for the Pd(II) binding on the NPs. Adopted from Ref. [147]



Scheme 11 A bis-TSC ligand anchored twice on a core(black)-shell(white) NP surface

TSC N^S chelate moiety. This is even true if further coordinating groups were introduced in TSC producing polydentate TSC ligands. Such polydentate TSCs have also the benefit, that although their –NHC = S– group is susceptible to thione-thiol tautomerism and thus the binding strength of this group might vary with the pH, proper choice of the other coordinating groups will allow to circumvent massive dependence of the binding capacities on the pH. Indeed, TSCs can bind with metal ions at a broad pH range and also retained the high adsorption capacity when anchored onto NPs. Therefore, TSC-functionalized adsorbents are very attractive for removing or recovering metal ions from aqueous solutions or sensing specific metal ions in solution.

Silica-based NPs including metal oxide@SiO_2 core@shell NP have turned out to be very versatile for the preparation of ligand-functionalized NP-based adsorbents, as functional groups on the surface can be easily introduced trough reactive silanes. These groups can then be used for covalent binding (conjugation) of the SiO_2 surface with suitable ligands, as has been shown for TSC, but also for other ligands.

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Declarations

Ethical Approval Not applicable.

Informed Consent Not applicable.

Conflict of interest There is no conflict of Interest.

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