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Recent advances in hexavalent chromium removal from aqueous solutions by adsorptive methods

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Chromium exists mainly in two forms in environmental matrices, namely, the hexavalent (Cr(VI)) and trivalent (Cr(III)) chromium. While Cr(III) is a micronutrient, Cr(VI) is a known carcinogen, and that warrants removal from environmental samples. Amongst the removal techniques reported in the literature, adsorption methods are viewed as superior to other methods because they use less chemicals; consequently, they are less toxic and easy to handle. Mitigation of chromium using adsorption methods has been achieved by exploiting the physical, chemical, and biological properties of Cr(VI) due to its dissolution tendencies in aqueous solutions. Many adsorbents, including synthetic polymers, activated carbons, biomass, graphene oxide, and nanoparticles as well as bioremediation, have been successfully applied in Cr(VI) remediation. Initially, adsorbents were used singly in their natural form, but recent literature shows that more composite materials are generated and applied. This review focused on the recent advances, insights, and project future directions for these adsorbents as well as compare and contrast the performances achieved by the mentioned adsorbents and their variants.

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1. Introduction

Over the past decades, the preparation and application of various adsorbent materials for the sequestration of toxic hexavalent chromium (Cr(VI)) from environmental samples have received vast attention from researchers across the world.[1–5] Chromium(VI) compounds, like hydrogen chromate ($HCrO_4^-$), chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$), owe their toxicity to the high solubility and diffusivity which permit them to cross the biological membrane tissues easily.[6,7] Cr(VI) is toxic even at parts per billion levels.[8] The anthropogenic sources of Cr(VI) compounds in environmental samples include seepage or careless disposal from the electroplating, dying, nuclear power, metal finishing, leather tanning, photography and textile industries.[9–14] Another environmentally significant chromium species is the trivalent chromium (Cr(III)) which is considered non-toxic at minute concentrations; however, at high concentration, it can be toxic.

Conventional methods such as chemical precipitation, ion exchange, reverse osmosis, coagulation, and adsorption have been used to remove metal ions from different matrices.[1,2,4,15–19] Amongst these methods, adsorption is viewed as superior to other methods because of its simplicity, ability for regeneration, cost-effectiveness, and enabling large-scale applications.[20,21]

Confiscation of Cr(VI) from aqueous solutions by adsorption methods has been accomplished by exploiting its physical (physisorption), chemical (chemisorption) and biological (bioremediation) properties due to its dissolution tendencies in aqueous solutions.[1,2] A plethora of adsorbents of different origins including synthetic polymers, activated carbons, biomass, graphene oxide, nanoparticles, and biosorbents have been investigated for Cr(VI) removal. Adsorbents are used in their native form, but the general trend lately has been that of modified adsorbents either by crosslinking, grafting, changing the chemical form or through engineered composite materials. Some adsorbents are used as scaffolds to generate new materials with improved functional groups (adsorption sites) in an adsorbent1@adsorbent2@adsorbent3 fashion. It has been reported that adsorption is limited by dominant functional groups on the surface and within the pores of an adsorbent.[22] Hence, the new general trend of re-functionalization of existing adsorbents. It is not a forgone conclusion that composite materials produce superior performance. For example, re-functionalization of activated carbons can result in the loss of carbon structure with the resultant carbon exhibiting pores that extend from one side to the other side of the particle surface. Such types of materials are not ideal for adsorption as they will mostly act as sieves than adsorbents. To date, researchers are striving to find suitable adsorbents for Cr with excellent adsorption capacity, selectivity, and faster binding kinetics while using the minimum dosage concentration. Recent literature shows a wide variability of adsorption performance for several adsorbents. Typical examples include Fe_3O_4@titanium residue, carbon-coated montmorillonite nanocomposite,

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electrospun carbon nanofiber mat which yielded the adsorption capacities (mg g^{-1}) of 14,[23] 100,[24] and 119,[25] respectively. The Fe_3O_4@titanium residue adsorbent exhibited superior selectivity for Cr(VI) in the presence of chloride, phosphate, sulphate, arsenite, and arsenate ions but its selectivity collapsed in a binary solution containing fluoride.[23] This is an indication that there is a room for new research in terms of adsorbent combinations to generate super adsorbents.

The demand for new or improved adsorbents has been sparked by the complex interactions of Cr(VI) with adsorbent functional groups leading to transformation of Cr(VI) to Cr(III), thus, incomplete removal of Cr. Consequently, four types of mechanistic interactions of Cr(VI) with biomaterials were identified.[26] The first scenario involves adsorption through electrostatic forces between positively charged adsorbent functional groups (*e.g.*, NH_4^+ or $COOH_2^+$) and anionic Cr(VI) species. The second mechanism pertains to adsorption of Cr(VI) onto the adsorbent surface, followed by a complete reduction of Cr(VI) to Cr(III). In the third situation, some fraction of anionic Cr(VI) is adsorbed while another fraction of Cr(VI) is reduced to Cr(III) followed by adsorption of Cr(III) on the surface of the biomaterial. A fraction of Cr(VI) is adsorbed while the other fraction is transformed to Cr(III) and released back into solution in the fourth scenario. The transformation (reduction) of Cr(VI) to Cr(III) can either be direct or indirect.[27] Direct conversion takes place when Cr(VI) ions are attached to adsorbent sites that can donate electrons (O, S, and N) to facilitate reduction. Besides, the presence of cations like Fe^{2+} on the adsorbent surface also aids in the reduction of Cr(VI) to Cr(III). Indirect reduction happens when Cr(VI) attached to an adsorption site is reduced by the electrons from adjacent functional groups. While Cr(VI) undergoes reduction to Cr(III), the adsorption sites get transformed (oxidized) and this hinders the reusability of adsorbents for Cr(VI) uptake, for instance, the conversion of hydroxyl to carboxyl groups. Even though some studies still disregard the effect of reduction,[21,28] there has been many studies that have accounted for the reduction possibility using several techniques like Fourier transform infrared spectroscopy, energy dispersive X-ray spectroscopy and X-ray photon electron spectroscopy (XPS) to show the oxidation of surface groups and/or presence of Cr^{3+} species.[15,16,29,30] In addition to the four mechanisms listed above, esterification and coupling reactions involving Cr(VI) ions and catechol have been reported.[31]

Conversion of Cr(VI) into Cr(III) on the surface of nanoscale zerovalent iron has been reported as the mechanism of removal.[3,32] The handling of the as-reduced Cr(III) by various studies has been different. While some attempted to explain the re-adsorption of Cr(III),[23,33,34] others were content with the fact that Cr(VI) was transformed to its less toxic form.[3,15,16,35,36] The neglect that high concentrations of Cr(III) is toxic could be detrimental. Besides the chemisorption processes mentioned, physisorption processes are also well-known particularly with materials possessing high surface area and large pore volumes like activated carbon, graphene oxide, and zeolites.

Recent review articles focusing on the use of different adsorbents in the removal of heavy metals, including Cr(VI) from aqueous solutions have emerged.[37–42] Most of these review articles focused on the application of specific adsorbents such as silica-based materials,[37] polypyrrole-based adsorbents,[38] advanced carbon nanotubes,[39] clay minerals,[40] functionalized carbon nanotubes, graphene[41] and nanomaterials in general.[42] Despite the extensive existence of adsorbents for Cr(VI) removal from aqueous solutions, new adsorbents, and modification of existing adsorbing materials have been recently reported.[3,43–50] Unlike in previous review articles,[37–41] this work focused on reviewing the major adsorbents reported in the literature (up to the year 2019) mainly for the removal of Cr(VI) from aqueous solutions. The objectives of this review included outlining some of the recent developments in the field of adsorption, where a trend of utilizing composites, particularly incorporating nanomaterials, has dominated the recent literature. Also, to provide one-stop resource material for Cr(VI) adsorption.

2. Adsorbent classification, characteristics and development history

Several classes of adsorbents including synthetic polymers, biopolymers, graphene-based, activated carbon (AC), silica and biosorbents, are used in Cr(VI) confiscation. Chitin and cellulose are the two most common biopolymers used in adsorption. Cellulose is a polysaccharide whose molecular weight hinges on the plant material it was extracted from as well as the purification procedure used.[51] Cellulose exhibit intrinsic characteristics, such as robustness, abundance, biodegradability, nontoxicity, mechanical, and thermal stability.[51,52] Also, cellulose is odourless water soluble linear polymer whose monomeric units of β-D-anhydroglucopyranose are covalently bonded *via* C^1–C^4 β-glycosidic linkages.[53] Its water solubility property is detrimental for its use as an adsorbent in raw form; hence, numerous functionalization procedures have been adopted. Graft and cross-linking modifications have dominated the research, but sophisticated functionalization such as those reported elsewhere[54,55] have shown promising results in Cr(VI) removal. Cellulose modified with β-cyclodextrin and quaternary amines demonstrated high adsorption rates and rebinding properties governed by the pseudo-second-order kinetic model.[56] Chitin is derived from shells of crustaceans like crab, crayfish, prawn, and shrimp. Due to the low adsorption performance of chitin, earlier research was concentrated on fabricating chitosan from chitin through deacetylation usually employing a strong base like NaOH to provide reactive sites enriched with NH_2 and OH functional groups.[57] Chemical modification of cellulose and chitosan with organic ligands and cross-linking[21,36,51,54,58,59] dominated earlier research but recently emphasis has been on the incorporation of nanomaterials into their backbone.[16,60,61] The latter has been reported to improve the adsorption performance for both adsorbents.

Another interesting class of adsorbents is the graphene oxide (GO) based adsorbents, mainly because of the abundant –OH, –COOH and –C=O functional groups on their surface imparted during oxidation of graphite.[62] The presence of such groups makes GO an ideal adsorbent for metal ion chelation and excellent hydrophilic properties owing to hydrogen bonding. However, its recovery from the water after adsorption is troublesome given its high dispersion in water. To avert that, GO have been used as building blocks of other adsorbents in composite manufacturing. As high as 539.53 mg g^{-1} adsorption capacity was reported for Cr(VI) removal using a composite material prepared from polyethyleneimine (PEI) and GO.[60] However, the adsorption equilibrium was reached after 14 h, demonstrating a need for further improvement in such types of adsorbents. Evaluation of the selectivity using solutions containing Ni(II), Cu(II), and Cd(II) cations was unjust because the mode of Cr(VI) removal by the GO–PEI adsorbent was described to proceed *via* electrostatic interaction between anionic Cr(VI) and protonated amine groups. Therefore, a repulsion of the cationic species was always going to be expected under conditions favouring electrostatic attraction of Cr(VI) to positively charged adsorbent sites. Anions, like sulphates, phosphates, nitrates, fluorides, and chlorides could have been explored.

The abundance, low cost, and presence of diverse functional groups (hydroxyl, carboxyl, carbonyl *etc.*) in agro-based byproducts such as shells and kernels elicit interest from scientists to investigate their potential application in the elimination of pollutants from water. However, low surface area and low adsorption performance limit their utilization in pristine form. For example, a solution containing 80 mg L^{-1} of Cr(VI) at pH 2 was treated with 2 g L^{-1} of pristine almond green hull and 99.94% removal efficiency was obtained[63] while 3 g L^{-1} adsorbent dosage concentration of *Hibiscus cannabinus* kenaf yielded a Langmuir monolayer adsorption capacity of 0.582 mg g^{-1} in 90 min of equilibration time at pH 7.[35] Given the high dosage concentrations used (2 and 3 g L^{-1}) in relatively low concentration of Cr(VI) (80 and 50 mg L^{-1}) clearly illustrates the limitation of utilizing raw biosorbents. Hence, research on the improvement of adsorption performance through various modifications of biosorbents is still ongoing.

The agro-waste materials also play a crucial role as precursors for AC manufacturing. ACs are highly carbonaceous materials possessing large surface area, high porosity, and high adsorption capacity.[64] Commercial ACs are costly and nonselective. Researchers continue to investigate alternative cheaper and more available sources of carbon, including plant materials, tyres, coal, bones, municipal waste *etc.* The heating method and the precursor used influence the final characteristics of ACs. Major research was concerned with improving the properties of the AC through investigating different heating and carbonization temperature as well as studying the influence of various activating agents and activation methods. ACs are highly hydrophobic and in turn, have achieved limited success in metal ion removal, including Cr(VI) as opposed to organic pollutants. Ecofriendly and low-cost ZnO-tetrapods/activated carbon (ZnO-T/AC) nanocomposite synthesized by the hydrothermal method were investigated for Cr(VI) adsorption and were found to provide high adsorption efficiency.[65] The ZnO-T/AC nanocomposite was designed to integrate the intrinsic properties of AC and nanoparticles. On the same token, there seems to be limited research on the study of activated carbon/nanoparticles/silica composite for the removal of Cr(VI). Investigation of magnetic nanoparticles supported on AC ($AC@Fe_3O_4@SiO_2–NH_2–COOH$)[66] as potential adsorbents for the decontamination of Cr(VI) is one of the few examples in this area. Promising Cr(VI) removal efficiency of 70% from water solution having a salinity of 20 000 ppm adjusted to pH 7 was reported.[66] Systems of this nature ($AC@Fe_3O_4@SiO_2–NH_2–COOH$) require skilled chemists for synthesis as they involve lots of steps and reagents. The inclusion of nanomaterials in adsorbents should be conducted in such a way to prevent leaching of nanoparticles during their use. Nanomaterials exhibiting high surface area, non-toxic, easy removal after sorption, and pronounced selectivity of pollutant at trace concentrations are desirable.[42]

Excitement over the application of mesoporous silica-based adsorbents was triggered by their excellent properties such as uniform pore structure consisting of well-defined pore size, high specific surface area, and larger pore size.[67–70] In Sharma *et al.*,[65] it was pointed out that complicated synthesis, longer reaction time needed for synthesis, separation difficulties coupled with the high cost of reagents has limited the practical applications of silica adsorbents. Cr(VI) recoveries between 91.9 and 103% from lake, rain, and river water were reported for carboxylic acid-functionalized mesoporous silica.[67] More details on the merits and demerits of various adsorbents can be found in the review by Mohan and Pittman.[71]

3. Toxicity of chromium

Even though Cr is known to exhibit several oxidation states, but only two forms, Cr(III) and Cr(VI), are of environmental importance. In the aqueous environment, Cr(III) may hydrolyze into several species including $Cr(OH)^{2+}$, $Cr(OH)_2^{+}$, $Cr(OH)_4^{-}$, neutral species $Cr(OH)_3^{-}$ and polynuclear species $Cr_2(OH)_2$ and $Cr_3(OH)_4^{5+}$.[63] These hydroxides are less mobile, soluble, and toxic to living organisms due to their tendency to form complexes with organic ligands (natural organic matter) in the environment.[72] Also, at minute concentrations, Cr(III) is needed for the metabolism of glucose, lipid and amino acids[2] with a recommended average amount per human body per day of 0.4–6 mg.[32] In humans, hair has been reported to be the highest accumulator for Cr compounds with concentrations ranging from 0.23 to 3.8 mg kg^{-1}.[2] The toxicity of Cr(III) compounds is not as well-documented as that of Cr(VI) compounds but suppression of the immune system activity[73] and red blood cells damage[74] have been reported. There has been a growing body of evidence narrating the possible conversion of Cr(III) to Cr(V) and subsequently to Cr(VI) compounds in the extracellular[75] and intracellular structures.[75,76] Lindsay and Farley[77] reported the reoxidation of Cr(III) to Cr(VI) during wastewater treatment by chlorination. This new evidence shows that the possible toxicity of Cr(III) compounds at high concentrations cannot be ignored. As such, few studies have focused on the adsorptive removal of Cr^{3+} from various matrices.[78,79]

On the other hand, Cr(VI) hydrolyzes to $Cr_2O_7^{2-}$, CrO_4^{2-} and $HCrO_4^{-}$ which are strong oxidants.[71] The Cr(VI) compounds are more mobile and soluble, making them bioavailable. The hexavalent Cr species are toxic as they are associated with a variety of detrimental health effects such as skin rash, weakened immune system, nose irritations and nosebleed, ulcers, allergic reactions, kidney and liver damage, genetic material alteration, gastric damage, and even deaths.[80] The toxicity of Cr(VI) on humans has been primarily accredited to the chemical structural resemblance between Cr oxyanions $[\mathrm{CrO_4}^{2-}]$ and sulphate ions $[\mathrm{SO_4}^{2-}]$ making the former able to cross the biological membranes using sulphate routes.[81] A detailed study reported by Wise *et al.*[82] showed that Cr(VI) is genotoxic to human urothelial cells, thereby inducing aneuploidy. The DNA damage was inflicted with low Cr(VI) concentrations varying from 0.5–3 μM.[83] Due to the aforementioned health effects related to Cr(VI) toxicity, numerous studies have focused on developing methods for the removal of Cr(VI) compounds from various matrices.

4. Removal of Cr(VI) from aqueous solutions

Water treatment technologies for Cr(VI) mitigation emphasize on removal, containment, and/or reduction.[2,84–86] Hence, some studies have capitalized on the solubility of Cr(VI) at all pH ranges by first reducing the Cr(VI) to its less toxic form of Cr(III) followed by precipitation.[2] Viti *et al.*[87] reported the reduction of Cr(VI) by H_2S to proceed *via* three steps: (i) reduction of sulphates, (ii) reduction of chromate by sulphides and (iii) precipitation of Cr(VI) by sulphide. Chemical precipitation is the most viable commercial method for the removal of metal ions, but it has not enjoyed an overwhelming application in the removal of Cr(VI) because chromates do not precipitate easily using the conventional methods.[88] Other challenges associated with chemical precipitation are the generation of sludge rich in toxic metal ions as secondary pollutants, water hardness, and slow reaction speed.[89] In this case, it is clear that Cr(VI) abatement strategies require more resources in terms of chemicals, equipment, and intensive labor. Another point in case is the filtration systems which require membranes that can be costly at times and additional chemicals needed to convert Cr(VI) into other forms. Elsewhere, prior to filtration, Cr(VI) was initially reduced with ferrous sulphate to Cr(III) followed by coagulation.[18] In a different study, three polymers (chitosan, polyethyleneimine, and pectin) were investigated for a polymer-enhanced ultrafiltration method required for the removal of Cr(VI) from aqueous solutions.[9] In their investigation, Aroua *et al.*[9] required an ultrafiltration system that was equipped with polysulfone hollow fiber membrane. In a different study, the application of plant species for abatement of Cr(VI) in irrigation water resulted in the conversion of hexavalent chromium to trivalent chromium in plant species (*Phragmites australis* and *Helianthus annuus*).[85] In any case, the total chromium removal reported using the two plant species ranged from 54% (*Phragmites australis*) to 70% (*Helianthus annuus*).[85] A simple conversion of Cr(VI) to its less toxic form of Cr(III) might not be a complete ideal solution for water that enters the environment due to the possibility of unknown environmental conditions that could reverse the situation. Thus, ion exchange and reverse osmosis are limited by their high cost, membrane fouling, and poor stability.[90,91] The current review focuses only on adsorption methods as applied in Cr(VI) removal.

4.1. Adsorption process

Adsorption refers to an accumulation of adsorbates at a surface of an adsorbent or the interface between two phases. Adsorption is mostly an exothermic process due to the decrease in surface energy of the adsorbent impelled by the inhibition of the adsorption site atoms' movement induced by the attachment of adsorbate molecules. Adsorbates may attach on the adsorbent through electrostatic attraction, ion exchange, ion-pair interactions, van der Waals forces, cation–π and hydrophobic hydration.[58,92] Adsorption could be described by physisorption and chemisorption processes. In physisorption, the bonding of adsorbates to the surface of adsorbent proceeds through weak reversible van der Waals forces while chemisorption takes place *via* chemical bonds that are mainly irreversible.[42] Some studies have postulated that adsorption of Cr(VI) by adsorbents is through electrostatic attractions,[15,93] adsorption, and reduction[16,23] or just plain adsorption.[63] The type and nature of adsorbent and its functional groups determine the mechanism of metal abstraction. The sections below detail how various adsorbents were fabricated to maximize their Cr(VI) uptake from aqueous media with more emphasis on recent trends adopted for the synthesis of adsorbents.

4.2. Application of various adsorbents for Cr(VI) removal

Adsorbents come in various formats including synthetic polymers, waste materials, nanomaterials, and biomaterials. The general rule is that the adsorbents must be insoluble in the solution that contains the analyte to be adsorbed and should contain high surface area with some porosity for physisorption and complementary functional groups for the chemisorption process. In addition, adsorbents must remain intact during the recovery of adsorbates, *i.e.*, should show mechanical stability in the presence of the desorbing medium. To meet such requirements, cross-linking reagents are utilized. Not only does cross-linking improves rigidity, stability, and ruggedness of adsorbents, but it also helps with the incorporation of functional groups necessary for metal abatement as well as serving as scaffolds for further functionalization, *e.g.*, grafting. The inclusion of new functional groups either through cross-linking or grafting enhances the selectivity during metal sequestration. In the case of polymers, size and length of monomers influence the performance in adsorption. Too bulky and longer alkane chains might cause steric hindrance and increased hydrophobicity of which both would lead to poor adsorption performance for metal ions. Therefore, careful consideration and matching of analyte chemistry to that of adsorbent surface functional groups is paramount for optimal performance.

4.2.1. Synthetic polymer-based adsorbents. Recently, the application of synthetic polymers as metal ion abstractors has been a subject of intense research.[35,54,92,94–96] Cross-linked poly(4-vinyl pyridine):divinylbenzene copolymers quaternized with amino groups were used as anion exchangers for the removal of Cr(VI).[35,97] The quaternized materials performed well in the removal of Cr(VI) from aqueous solutions, but a slight reduction in adsorption performance was observed in the presence of sulphate ions. Kalidhasan *et al.*[92] developed a highly efficient adsorbent for Cr(VI) sequestration by impregnating Amberlite XAD, a synthetic polymer, with tetraoctylammonium bromide (ionic liquid). A Langmuir adsorption capacity of 196.1 mg g^{-1} was reported, and the enhanced removal of Cr(VI) was attributed to the pivotal role played by ion-pair, electrostatic, cation–π, van der Waals and hydrophobic hydration interactions between sorbate and adsorbent.[92]

Elsewhere, ion-imprinted polymers (IIPs) were utilized to improve the removal of Cr(VI) in the presence of co-ions.[98,99] IIPs are defined as materials synthesized by incorporating the analyte as a template during synthesis resulting in a polymer with cavities mimicking the shape, charge, size, and functionality of the template ion. In this context, Pakade *et al.*[98] synthesized a Cr(VI)-IIP from a copolymer of 2-vinyl pyridine and 4-vinyl pyridine containing styrene monomers as spacers to accommodate the bulkiness of Cr(VI) induced by the oxygen atoms around Cr. The prepared IIP exhibited superior selectivity of Cr(VI) against ten-fold high concentration of sulphates from acid mine drainage water sample compared to its control (non-imprinted polymer (NIP)). In a different study, Bayramoglu and Arica[99] prepared a Cr(VI)-imprinted polymer from poly(4-vinyl pyridine-*co*-hydroxyethyl methacrylate) co-monomers. The synthesized IIP exhibited a maximum adsorption capacity of 172 mg g^{-1}. Adsorption equilibrium was reached within 40 min, illustrating that the process was faster and was explained by pseudo-second-order kinetic mechanism. IIP for Cr(VI) was selective in the presence of Cr(III) and Ni(II). Even though IIPs have exhibited superior selectivity towards Cr(VI) with excellent adsorption capacities, the unavailability of commercial sorbents is still an issue of concern. Hence, new sorbents with improved performance are continually sought after.

In a detailed review on the use of different types of adsorbents for Cr(VI) sequestration, it was projected that the application of adsorbents modified with nanomaterials could be an area of intense research.[100] Indeed, this has been the case, judging by the publications discussed in this work. Taghizadeh and Hassanpour[94] prepared a Cr(VI)-IIP anchored on magnetic multi-walled carbon nanotubes *via* precipitation polymerization employing 4-vinyl pyridine (4-VP) and 2-hydroxyethyl methacrylate (HEMA) co-monomers. The reported maximum adsorption capacity reached after 30 min of equilibration was 56.1 mg g^{-1}, and the polymer demonstrated a high single selectivity sorption for the Cr(VI) ions in the presence of competing ions (Cu^{2+}, Ni^{2+}, F^-, NO_3^- and SO_4^{2-}) but nitrate was the prevalent competitor.[94] It has to be noted that, the anchoring of 4-VP and HEMA on magnetic multi-walled carbon nanotubes yielded a polymer with lesser performance (56.1 mg g^{-1} (ref. 94) *vs.* 172 mg g^{-1} (ref. 99)) compared to the simple IIP prepared from the same functional monomers. The added cost of synthesizing the magnetic multiwalled carbon nanotubes plus the inferior adsorptive performance make the new method not ideal. Probably, the magnetic multiwalled carbon nanotubes owing to hydrophobicity were not involved in Cr(VI) abatement or the adsorption sites were not easily accessible, hence lower adsorption capacity.

Liang *et al.* also employed 4-VP and HEMA co-monomers for the synthesis of magnetic Cr(VI) IIP, but the polymer was supported on silica nanoparticles.[101] The use of silica nanoparticles tremendously improved the adsorption performance of the polymer by almost 6-folds (up to 311.95 mg g^{-1}). This could be attributed to the high surface area to volume ratio displayed by nanoparticles in relation to multi-walled carbon nanotubes. A combination of vinylimidazole and 3-aminopropyltriethoxysilane co-monomers was utilized to produce a Cr(VI) IIP imprinted on the surface of magnetic nanoparticles.[102] The reliability and feasibility of the prepared IIPs were evaluated with real samples, tap water, lake water and river water with a limit of detection ($C_{\mathrm{LOD}} = 3S_{\mathrm{b}}/m$) of 0.29 ng mL^{-1}. Velempini *et al.*[54] prepared Cr(VI)-imprinted polymer by cross-linking carboxymethylcellulose-ethylenediamine with epichlorohydrin. The maximum adsorption capacity described by a Langmuir isotherm was found to be 177.62 mg g^{-1} at 25 °C and sulphate was reported to be the highest competitor. In the latest work, the researchers have been able to achieve high adsorption capacities and selectivity with their materials. This indicates that a careful selection of a set of monomers and their assimilation to magnetic nanoparticles immobilized to some form of support (*e.g.*, carbon, nanoparticles, graphene oxide, and cellulose) could be the future direction for producing high efficient Cr(VI) IIPs, but silica nanoparticles seem to give best results.

4.2.2. Natural polymer-based adsorbents. Adsorption employing biopolymers is among the recommended methods for the treatment of metal ion pollutants due to the low cost of biomaterials, high effectiveness, minimum chemicals needed, and regeneration opportunities.[59–61,103,104] Natural polymers like cellulose, chitin, and chitosan have been used for trace metal mitigation for decades. Chitosan contains chemical functional groups, like NH_2 and OH, that can aid in trace metal sequestration and complexation, while cellulose is a polysaccharide mostly dominated by OH^- and CHO^- groups. Mainly, the modifications of chitosan can be by physical methods (changing from flakes to beads), or chemical methods where cross-linking or grafting functional groups is carried out.[21,59,104–106] Recently, more composite materials incorporating chitosan backbone have been reported.[60,61] Preethi *et al.*[15] synthesized biopolymers assisted oxyhydroxide materials, aluminum–lanthanum mixed oxyhydroxide (ALMOH) and chitosan/aluminum–lanthanum mixed oxyhydroxide (CSALMOH), and evaluated them for Cr(VI) removal. The maximum adsorption capacities reported were 49.80 and 78.90 mg g^{-1} for ALMOH and CSALMOH, respectively. The sulphate and the carbonate were found to be the most significant competitors for Cr(VI) adsorption, and the overall selectivity order was $SO_4^{2-} > HCO_3^- > NO_3^- > PO_4^{3-} > Cl^-$.[15] Bhatt *et al.* experimented the trimesic acid-cross-linked chitosan for the adsorption of Cr(VI).[58] Ionic, π–π and hydrogen bonding interactions were described as the forces of recognition that participated in the abstraction of the metal ion resulting in adsorption capacity of 129.53 mg g^{-1} from an equilibrium concentration of

336.63 mg L^{-1} but after a very long contact time of 882.5 min. Such long equilibration time could be detrimental for the employment of the adsorbent in industrial applications. Gopal Reddi *et al.*[21] investigated the removal of copper and chromium from aqueous solutions using chitosan-*g*-maleic anhydride-*g*-ethylene dimethacrylate adsorbent. The double grafted copolymer of chitosan demonstrated excellent removal capabilities. An adsorption loading of 266.67 mg g^{-1} was reported for the removal of Cr(VI) by ionic liquid impregnated phosphate chitosan adsorbents.[16] It has been reported that superior adsorption performances can be achieved by the modification of both the structure and the functional groups on the adsorbent.[16] The structural modification was achieved by cross-linking the chitosan with phosphate while ionic solid ethylhexadecyldimethylammonium bromide was used to functionalize the material. The high adsorption capacities achieved with the modified chitosan adsorbents pointed to the synergistic effects of composite materials and their advantages over individual materials. Biocompatible magnetic nanoparticles imprinted cellulose composites were synthesized for the remediation of Cr(VI) from aqueous solutions.[55] In this study, three different adsorbents, nanoparticles, cellulose and hydrotalcite or hydroxyapatite (a double-layered hydroxide), were used to fabricate a biocompatible material of the three-layered structure, Fe_3O_4@cellulose@double layered hydroxide. It was found that the three-layered adsorbents performed better than the corresponding two-layered adsorbents, Fe_3O_4@cellulose or cellulose@double layered hydroxide, with adsorption capacities ranging from 25.259–28.739 mg g^{-1}. The selectivity of the prepared three-layered adsorbents was negatively affected by the presence of carbonates (HCO_3^-) particularly because of the tendency of HCO_3^- to increase the pH of solution leading to diminished active sites.[55] However, this engineered combination did not produce an adsorbent with higher capacity in comparison to, say the ionic liquid impregnated sorbents reported elsewhere.[16] It also goes to show that complexity does not always yield better performance. Therefore, in as much as researchers modify or create these composite adsorbents, performance *versus* cost need to be considered all the time for the adsorption process to remain highly efficient, simple, and cost-effective.

4.2.3. Application of bio-adsorbents for Cr(VI) adsorption. The continued challenge of getting alternative biosorbent materials that are cost-effective and efficient have opened avenues for researchers to try almost any material of plant origin in adsorption of metal ions.[1] Lignin, hemicellulose, and cellulose are the major components of biomaterials responsible for metal chelation/complexation and ion exchange during application of such adsorbents.[107] Besides the bulky structures of lignin, cellulose, tannins, and hemicellulose as well as trace metal ions, biomaterials possess a cornucopia of functional groups like aldehydes, ethers, alcohols, ketones, and esters.[108] Owing to their abundant availability, biodegradability and cheap cost, numerous biosorbents from different sources, *Macadamia* nutshells,[108] pine cone biomass,[109] *Cannabinus* kenaf,[35] Masau stones,[34] sawdust,[6] almond green hull,[63] grape peelings,[110] lemon peel powder,[111] coir pith[112] and fungal biomass[113] have been successfully used for the adsorption of Cr(VI). Despite the breakthroughs made in using native biosorbent materials, low surface area, low adsorption capacities, high chemical, and biological oxygen demand, as well as total organic carbon caused by leaching of organic components, remain the main drawbacks of applying biosorbents in their raw form.[114,115]

Several treatment methods have been proposed to address these limitations. These include biological treatment with bacteria or fungi, chemical treatment (or bleaching) with an alkaline solution, and oxidizing agents, physical treatment methods like mechanical agitation or sonication, and physicochemical methods such as steam explosion.[108] In addition to the above, cross-linking, grafting, converting to activated carbon or fabricating biocomposites are usually the secondary treatments undertaken.[62,65,67,68,70,72] Recent literature has revealed that new or alternative adsorbents for the removal of Cr(VI) are experimented.[35,63,116] The limitation of biomaterials is the poor surface area, and as such, they are rarely used as scaffolds for preparing composite adsorbents of the type adsorbent1@adsorbent2@adsorbent3 format. New literature on this field mainly focuses on cross-linking coupled grafting. In addition, biomaterials are mainly used as precursors in the production of activated carbons. The typical study, Masau stones cross-linked with epichlorohydrin (ECH) and grafted with diethylenetriamine (DETA) were experimented for the removal of Cr(VI) from aqueous solutions.[34] The adsorption capacity of 87.33 mg g^{-1} was achieved within 250 min. A complex mechanism of removal involving adsorption of Cr(VI) through electrostatic attraction, hydrogen bonding, and π–π interactions was reported.[34] Application of lignocellulose-based materials in metal ion confiscation has been covered in several recent reviews.[1,2,114,115,117] Hence, the current review will not attempt to repeat those reviews but will instead focus on the overall trend in adsorbent synthesis and application.

4.2.4. Carbon-based adsorbents. Review articles have been presented on the application of AC in the remediation of pollutants such as chromium from water since over a decade ago.[71,118] This implies that there is a strong potential for the usage of AC in the removal of chromium from water. The preparation of the AC is usually performed by the carbonization of the raw material at temperatures below 800 °C in the absence of oxygen followed by the activation of the carbonized product (char), which is done either physically or chemically.[117,118] Commercial ACs are expensive, and this has led to the generation of low-cost adsorbent by many researchers using waste materials.[118–122] Some ACs used for the removal of Cr(VI) from aqueous solutions recently were derived from fox nutshell,[119] wood apple shell,[120] mango kernel[121] and termite feces.[122] The AC adsorbents showed good recognition ability for Cr(VI) removal from aqueous solutions with an adsorption capacity of up to 315 mg g^{-1}.[123] For example, the adsorption capacities of Cr(VI) at pH 3.0 and temperature of 40 °C were 315 and 186 mg g^{-1} for the KOH-activated and acid-activated (Acticarbone) carbons, respectively.[123] In the same context, the maximum adsorption capacity achieved by Acharya *et al.*[124] for mitigation of Cr(VI) from wastewater by AC developed from Tamarind wood activated with zinc chloride was 28.019 mg g^{-1}. Several investigations have shown that the maximum removal of Cr(VI) from aqueous solutions occurs at acidic conditions probably due to the neutralization of negative charges on the surface of the adsorbents by excess hydrogen ions, thereby enabling the diffusion of hydrogen chromate ions ($HCrO_4^-$) and their subsequent adsorption.[121,123]

In addition to using the as-prepared AC, new literature has emerged where re-activation, modification, and functionalization process of the native AC were undertaken.[125–131] The post-treatment of AC allows for the addition of new functional groups, increase the amount of existing functional groups, changing from one form to another (*e.g.*, from thiol to amino) or improve on the physical attributes such as specific surface area, pore-volume, and pore size. Functional groups bearing oxygen atoms (phenolic hydroxyl, carbonyl or carboxyl groups) were produced by chemical oxidation of AC.[126,132] Oxidizing agents including H_3PO_4,[133] HNO_3,[125] and $KMnO_4$ (ref. 127) and activating agents such as HCl,[134] cationic surfactant[135] as well as peracetic acid[126] were employed for oxidative post-treatment of AC. Amination of epichlorohydrin cross-linked AC yielded a Langmuir monolayer adsorption capacity of 145 mg g^{-1}.[136] In addition to cross-linking and grafting, AC are used as supports for producing much complex systems of the adsorbent1@adsorbent2@adsorbent3. A typical study of the three-level adsorbent composite prepared from carbon@ferrous sulfide@iron showed potential in the removal of Cr(VI) from aqueous solution.[72] It should be emphasized that AC does not only act as support, but it can also partake in the adsorption either through physisorption (owing to their large surface areas) or chemisorption (due to the presence of heteroatoms on the surface). Particularly, for Cr(VI) removal, the heteroatoms participate in the reduction process.

Besides AC, biochar and carbon nanotubes are other carbon variants that have been experimented for Cr(VI) adsorption. *Ab initio* studies demonstrated that carbon nanotubes functionalized with titanium complexes could be potential adsorbents for Cr(VI) removal due to the large specific surface area, structural diversity, good chemical stability, small size, possible regeneration low density and reusability.[137] Recently, commercial carbon nanotubes modified with hydrogen peroxide were experimented for Cr(VI) adsorption, and the energies of adsorption obtained from the Dubinin–Radushkevich isotherm ranging between 0.371 kJ mol^{-1} and 0.870 kJ mol^{-1} indicated that the process was through physisorption.[138] A composite material prepared from AC/Fe_3O_4/SiO_2 capped with amine and carboxylic groups exhibited good recognition of Cr(VI) in the presence of Pb(II).[66] The inclusion of nanoparticles in composite fabrication seems to bring beneficial results and adsorbent composite performance enhancement. Magnetite nanoparticles have been widely explored by many researchers chiefly because not only do they offer quick and easy separation with the aid of an external magnet but also their adsorption capacity and inherent large surface area.[66] Exploration of other nanomaterials for Cr(VI) decontamination has also emerged.

4.2.5. Nanomaterial based adsorbents. Nanomaterials are defined as materials and structures having a particle size diameter of 1 to 100 nm, at least in one dimension possessing unique optical, mechanical, and magnetic properties.[42] Due to the large surface area to volume ratio, nanomaterials have attracted an overwhelming interest as adsorbents. Use of bare nanoparticles in adsorption is problematic owing to difficulties in separating them from aqueous solution after adsorption. To address such challenges, recent literature has concentrated on coupling nanoparticles with other adsorbents to prepare composite materials.[43] Dinari and Haghighi[139] synthesized nanocomposites on aromatic polyamide and modified ZnO nanoparticles for removal of Cr(VI) from water. The improved removal of Cr(VI) was credited to the *s*-triazine heterocyclic rings and silane coupling agent attached on the surface of ZnO nanoparticles. The schematic representation showing the preparation of modified ZnO nanoparticles modified by 1,3,5-triazine core silane coupling agent is presented in Fig. 1.

Ren *et al.*[23] successfully synthesized porous magnetite nanoparticles by reducing titanium residue with pyrite under N_2 atmosphere. The porous magnetite particles had a surface area of about 11.2 m^2 g^{-1} and the Langmuir adsorption capacity of 14.49 mg g^{-1}. The Cr(VI) was adsorbed and reduced to Cr(III) by the electrons in the system, and in turn, Fe(II) was oxidized to Fe(III) in the process. Dima *et al.*[60] experimented the removal of Cr(VI) by reticulated chitosan micro/nanoparticles (MCH) synthesized by inducing the gelation of a chitosan solution with tripolyphosphate (TPP), a non-toxic polyanion. The particle size had an average diameter of 100 nm. Cross-linking of MCH particles with TPP improved the removal performance due to the prevention of leaching of chitosan particles. Li *et al.*[22] synthesized chitosan nanofibers with an average diameter of 75 nm by electrospinning. An improvement in adsorption capacity from 26.7 to 68.3 mg g^{-1} compared to non-electrospun chitosan particles was achieved. The nanofibers showed greater recognition of Cr(VI) in the presence of NO_3^-, Cl^-, Na^+, Ca^{2+}, and Mg^{2+}, but were negatively affected by the presence of SO_4^{2-}. The lower adsorption in the presence of SO_4^{2-} was attributed to the tendency of SO_4^{2-} ions to cross-link with protonated amino groups, thereby decreasing the number of the binding sites of chitosan.[140] A novel material consisting of composite nanofibers (PAN–CNT/TiO_2–NH_2) was prepared by electrospinning polyacrylonitrile (PAN) and carbon nanotube (CNTs)/titanium dioxide (TiO_2) nanoparticles functionalized with amine groups (TiO_2–NH_2).[30] Excellent adsorption capacity of 714.27 mg g^{-1} was achieved. This is promising considering the equilibrium time was only 30 min and the initial Cr(VI) concentration was 180 mg L^{-1} adjusted to pH 2. This is a typical system of adsorbent1@adsorbent1@adsorbent2@adsorbent3@adsorbent4 where the ends (adsorbent 1 and 4) carry amino groups that have a high affinity for Cr(VI). It seems four and higher layered adsorbents could be the future judging by the astonishing adsorption capacity achieved.

Nanoscale zerovalent iron (nZVI) has been used for decades in metal ion treatment owing to its low standard redox potential of $E^\circ = -0.44$ V making it an efficient reductant upon contact with oxidizing agents like Cr(VI), thus reduced to Cr(III).[141] This interest in the use of ZVI could only spell its success in remediating pollutants. Numerous modifications have been

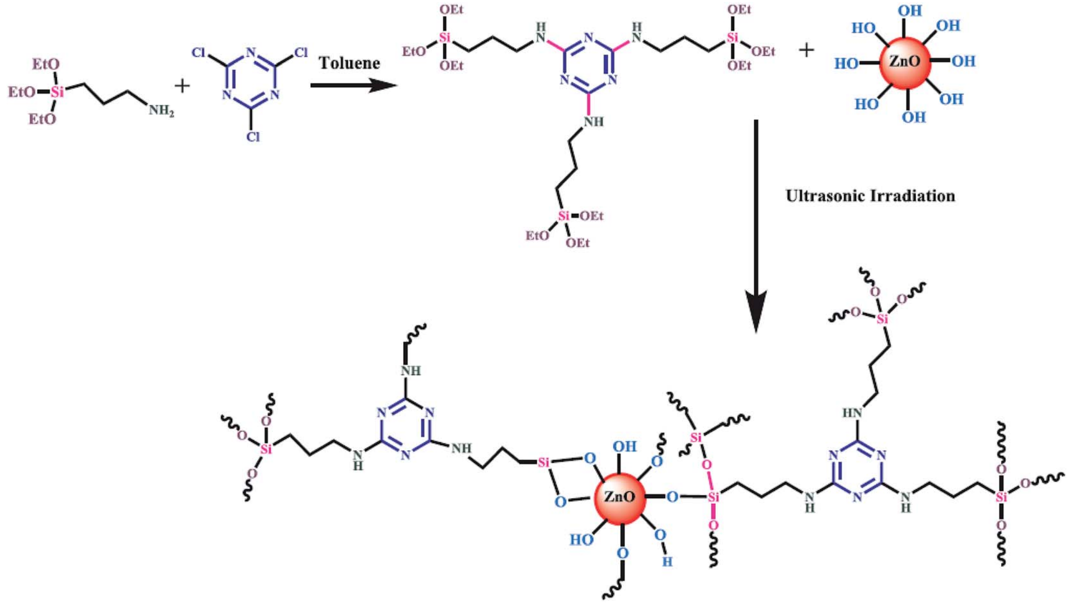

Fig. 1 Surface modification of ZnO nanoparticles by 1,3,5-triazine core silane coupling agent.[139]

reported[141] including immobilization of nZVI onto supports (activated carbon,[3] waste rock[4]), doping of ZVI with other metals bimetallic systems,[142] and combination of ZVI with Fenton-based oxidation. Bimetallic systems have mainly been applied for the dehalogenation of chlorinated organic compounds[141] as opposed to Cr(VI) mitigation. The latest work reported in the literature for removal of Cr(VI) from aqueous solutions includes the application of nanomaterials as adsorbents which include core–shell bimagnetic nanoparticles ($CoFe_2O_4@\gamma\text{-}Fe_2O_3$)[143] and magnetic arginine-functionalized polypyrrole nanocomposite.[144] A full review on the removal of chromium by nanomaterials can be accessed from ref. 42.

4.2.6. Silica-based adsorbents. Various reports on adsorption of Cr(VI) using silica-based adsorbents have been critically reviewed by Dinker and Kulkarni.[37] Hence, the present review discusses the most important findings and recent contributions. Due to their high specific surface area, well-defined pore size and larger pore volume, mesoporous silica materials have been utilized as supports for numerous applications.[68–70] In earlier modifications, silica particles were coated with synthetic polymers[70] or natural polymers like chitosan[145,146] in an adsorbent1@adsorbent2 composition. Recent literature has revealed that the modifications have advanced a step further, where preparation of adsorbent1@adsorbent2@adsorbent3 usually involves silica, polymer and a ligand or nanoparticles. A typical example is a thermo-responsive polymer (MS@APTES@PNIPAm) synthesized by grafting mesoporous silica materials with dual functional reactive agents, 3-aminopropyltriethoxysilane (APTES) and *N*-isopropyl acrylamide (NIPAm).[147] The MS@APTES@PNIPAm adsorbent showed good recognition ability for Cr(VI) removal with an adsorption capacity of 123.8 mg g^{-1}. The adsorption process was described by pseudo-second-order and intraparticle diffusion models. Although the equilibration time was relatively long (360 min) but impressive was the low adsorbent dosage concentration (0.2 g L^{-1}) used for a 30 mg L^{-1} initial Cr(VI) concentration. Elsewhere, treatment of mesoporous silica embedded with magnetite nanoparticles yielded an adsorbent with 50.51 mg g^{-1} adsorption capacity.[148] In this case, it was clear that the grafting of a thermos-responsive polymer (PNIPAm) vastly improved the capability of Cr(VI) removal by mesoporous silica.

The adsorption of Cr(VI) from aqueous solutions using silica-based adsorbent has been reported to be greatly influenced by the pH of the solution.[149] In this case, Qiu *et al.*[149] achieved the maximum adsorption capacity of 68 mg g^{-1} when the solution pH ranged from 2.5–5 due to electrostatic attraction between the $HCrO_4^-$ ions and the adsorbent, whereas, the maximum adsorption capacities of polymer functionalized silica materials were observed at pH 4 in a different study.[150] In this instance, the nature of the adsorbent plays a crucial role for adsorption as Cr(VI) exist in various forms depending on the pH; such that H_2CrO_4 exists at pH less than 1, while $HCrO_4^-$ prevails in the pH range of 1.0–6.0, and when the pH exceeds 7, CrO_4^{2-} is formed in solution.[71,149,150]

4.2.7. Graphene-based adsorbents. Graphene is a porous material made of carbon atoms with reported theoretical surface area values of up to 2630 m^2 g^{-1}.[89,151] Lack of heteroatoms in graphene makes it poorly soluble in water due to the absence of hydrogen bonding. Thus, despite the high surface area, graphene is a poor adsorbent due to inferior boundary layer needed for metal diffusion into pores. To improve the adsorption performance, numerous research has focused on the oxidation of graphite to graphene oxide (GO) and reduced graphene oxide (RGO) using the Hummers' method or its modifications. On that note, GO and RGO have enjoyed more applications in adsorption due to the presence of oxygenated functional groups such as hydroxyl, carboxyl, and epoxy groups on their surface.[89] These groups are pivotal for metal ion binding. Although RGO and GO possess characteristically high surface areas, when used in their pristine form, they tend to restack and agglomerate owing to π–π interactions between sheets leading inferior adsorption performance.[62] These limitations have been addressed by integrating other materials such as nanoparticles and organic ligands into the structural backbone of RGO and GO as demonstrated elsewhere.[151–154] Numerous modifications of GO and RGO have been reported for the elimination of hexavalent chromium.[45,55,151–153] RGO–Fe_3O_4 nanocomposites prepared by a solvothermal method were evaluated for the removal of hexavalent chromium.[153] Ma *et al.*[151] prepared and evaluated ethylenediamine–RGO (ED–RGO) for the removal of Cr(VI). The adsorption capacity achieved was 80 mg g^{-1}. An improvement of adsorption capacity to 92.15 mg g^{-1} was achieved when Zhang *et al.*[105] slightly modified Ma *et al.*[151] method by incorporating dimethylformamide (DMF) to produce ED–DMF–RGO. Another type of adsorbent1@adsorbent2@adsorbent3 experimented by Li *et al.*[154] for the removal of Cr(VI). The adsorbent was prepared from magnetic mesoporous titanium dioxide–graphene oxide core–shell microspheres and 117.94 mg g^{-1} sorption capacity was achieved at pH 6.5. Zhang *et al.*[89] demonstrated the applicability of RGO/NiO nanocomposites synthesized *via* a facile method for their adsorption of Cr(VI) from aqueous solution. The materials showed maximum performance at pH 4, reaching adsorption capacity of 198 mg g^{-1}. The adsorption performance achieved in Zhang *et al.*[89] with adsorbent1@adsorbent2 composition was better than that reported by a 3-level format in ref. 146 and 94. It still goes to show that chemical compatibility is vital.

4.2.8. Hierarchical porous carbon adsorbents. Some researchers have focused on producing ordered 3D structures with improved access to the adsorption sites and better mass transfer.[155,156] Hierarchical porous carbon adsorbent with 3D interconnected structure was prepared from a three-system precursor of resorcinol–melamine–formaldehyde anchored on nanocrystalline cellulose through a sol–gel process.[157] The material exhibited a higher adsorption capacity of 463 mg g^{-1} at pH 1 when evaluated for Cr(VI) removal with a batch method. The higher efficiency was attributed to the well-developed porous structure and large surface area of 1808 m^2 g^{-1}. The hierarchical porous carbon doped with nitrogen prepared from silkworm cocoon showed high performance for the removal of Cr(VI) from aqueous solution.[158] Porous flower-like hierarchical nanostructure SnS_2 (nanosheets) synthesized by heating a mixture of $SnCl_2 \cdot 2H_2O$ and thiourea at 170 °C in the presence of air for 2 h demonstrated superior adsorption and photocatalytic reduction properties for the hexavalent chromium in aqueous solution compared to SnS_2 nanoparticles and hydrothermally treated g-C_3N_4.[159]

4.2.9. Synergistic materials. Due to the complex nature of Cr(VI)-adsorbent interactions mentioned earlier, researchers have found ways to capitalize on the different interactions by producing adsorbents that address two or more mechanisms. Adsorption–reduction mechanism has been exploited by many researchers,[16,29,30,147,148,158] and examples from the literature are detailed below. Another synergistic Cr(VI) removal methods are the adsorption/catalysis/reduction.[160,161]

4.2.9.1. Adsorption/reduction. The synergy in adsorption and reduction during the removal of Cr(VI) by adsorbents has been mentioned by several researchers.[16,29,30,44,162,163] Anionic Cr(VI) could be adsorbed through electrostatic bonding on protonated sites or through anion exchange. The strong oxidant nature of Cr(VI) causes the surface where it was bonded to be oxidized while itself is reduced to Cr(III). Acidic conditions and existence of electrons catalyze this reduction. As mentioned previously, heteroatoms O, N and S carry those electrons. The transformation of Cr(VI) to Cr(III) under redox conditions is shown in eqn (1) and (2) with possible formation of an insoluble precipitate $Cr(OH)_3$ at basic pH.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O,\ E_0 = 1.33\ V \tag{1}$$

$$Cr_2O_7^{2-} + 4H_2O + 3e^- \rightarrow Cr(OH)_3 + 5OH^-,\ E_0 = -0.13\ V \tag{2}$$

Two possible mechanisms of reduction have been identified, mechanism I and II shown in Fig. 2.[113] Mechanism I is a direct reduction of Cr(VI) to Cr(III) where electrons are provided by the adsorption site. Mechanism II is an indirect reduction where an adsorbed Cr(VI) species receives electrons from an adjacent site to facilitate the reduction. Besides, reductants like sulfides, ferrous iron, thiosulphate, zerovalent iron, and C/FeS/Fe composites have also been used.[18,72,164,165] Several studies have accounted for the reduction of Cr(VI) during adsorption[3,4,16,30,32,166,167] while others have ignored.[21,54,92,147,148,158,168,169] Energy-dispersive X-ray spectroscopy and X-ray photoelectron spectroscopy (XPS) has been used to account for the presence or absence of Cr(III) in the surface of adsorbents after adsorption.[15,16,29,30] Atomic absorption spectroscopy can be used to account for Cr(III) in solution even though it does not measure it directly but rather calculated from the total chromium determination. The tendency of Cr(VI) to get reduced to Cr(III) imply that only quantifying Cr(VI) left in solution after adsorption could lead to inaccurate results. Therefore, researchers need to ascertain whether there was any Cr(III) in solution after adsorption.

4.2.9.2. Adsorption/catalysis. The application of photocatalytic procedures for the removal of Cr(VI) from aqueous solutions has been reported in the literature.[160] In this case, a biocatalyst synthesized from TiO_2-impregnated chitosan/xylan hybrid film was applied for photocatalytic reduction of Cr(VI) at a rate of 0.56 × 10^{-3} ppm min^{-1} in aqueous solution under ultraviolet irradiation.[160] Adsorption ability of hybrid film was due to ionic interactions based on the protonation of the amino group ($-NH_3^+$) on its surface, which resulted in highest adsorption (53.22%) occurring at pH 3. In a different study, chromium from water was removed using Mn_3O_4@ZnO/Mn_3O_4 composite under simulated sunlight irradiation.[22] The authors performed photocatalysis and adsorption concurrently and achieved 92% Cr removal efficiency within 70 min that was better compared to 88.8% achieved within 120 min in the separate two processes. Elsewhere, g-C_3N_4 nanosheets and a graphene three-dimensional (3D) gel system composed of two metal-free nano-sheets of g-C_3N_4 and graphene were capable of removing Cr(VI) *via* the synergistic effect of adsorption and

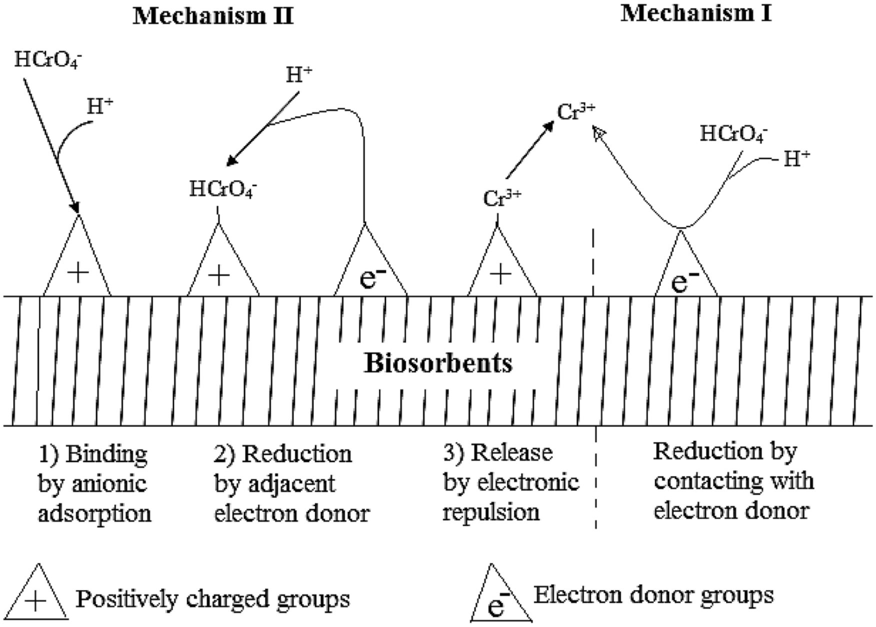

Fig. 2 Adsorption reduction mechanism of Cr(VI) by direct and indirect methods.[113]

photocatalysis.[161] The composite adsorbed 80% Cr(VI) (30 mg L^{-1}) in 30 min.[161] Studies in photocatalytic reduction of Cr(VI) and adsorption process of Cr(III) have indicated that these processes are pH-dependent with maximum Cr removal occurring in acidic conditions depending on the surface charge of the adsorbent.[160] This could be explained by the variations in the species of Cr(VI) over the pH range (1–14), where at pH = 3.0 for example, Cr exist as $HCrO_4^-$, which changes to CrO_4^{2-} as the pH increases.

4.3. Mechanisms of chromium removal (advancement in interpretation)

Due to the nature and intricacy of the adsorbents used in Cr(VI) removal over the past, several mechanisms for its elimination in water have been reported. Ng *et al.*[170] revisited the adsorption–reduction mechanisms mentioned in the four scenarios in the introduction. The first scenario which concerns only about the adsorption of anionic Cr(VI) through electrostatic attraction appears to be inconclusive and lack the in-depth understanding for the sorption of Cr(VI) compounds according to Ng *et al.*[170] Researchers going for this type of mechanism need to disprove the existence of Cr(III) in solution and on the adsorbent surface. In the second scenario where there is adsorption of Cr(VI) followed by complete reduction of Cr(VI) to Cr(III), the challenge is the sludge formed as a result of recovering the Cr(III) through precipitation. In the third scenario where Cr(VI) is adsorbed by the protonated sites at low pH followed by adsorption of the chelated Cr(III) species, the challenge is the proof of the chelation claim *versus* the repulsion of Cr^{3+} by the protonated sites. The greenish colour in the Cr-loaded adsorbent has been used to vouch for the anionic and cationic simultaneous adsorption by Hasan *et al.*[171] but the qualitative evaluation is not enough. Besides the dominant adsorption–reduction mechanism, recent studies have reported three mechanisms all taking place simultaneously, ion-exchange, electrostatic attraction, and reduction.[34,36] The ion exchange mechanism was explained on the basis of the presence of CO_3^{2-} in the interlayer structures of magnetic particles imprinted cellulose-based biocomposites made from hydrotalcite (HT) and hydroxyapatite (Hap).[36] The electrostatic attraction of chromate anions to the adsorbent's surface could be the result of the presence of higher valence cations like Ca^{2+}, Mg^{2+} and Fe^{3+} in the adsorbent[36] as indicated in Fig. 3 and/or protonated sites (OH_2^+, CN^+, NH_3^+) and quaternary amines (NR_3^+).[34] With such a complex mechanism all taking place simultaneously, the challenge could be getting a suitable solvent for the recovery of adsorbed Cr(VI). Both groups of authors did not perform desorption studies. Instant adsorption and reduction of Cr(VI) to Cr(III) while Fe^0 was oxidized to Fe^{3+} followed by precipitation of Cr^{3+} and Fe^{3+} as hydroxides were reported to be the dominant mechanism of removal with nZVI.[141] The overall mechanism was represented by eqn (3) and (4).

$$Cr_2O_7^{2-} + 2Fe + 14H^+ \rightarrow 2Cr^{3+} + 2Fe^{3+} + 7H_2O \quad (3)$$

$$Cr^{3+} + Fe^{3+} + 6OH^- \rightarrow Cr(OH)_3\downarrow + Fe(OH)_3\downarrow \quad (4)$$

Two other notable mechanisms involving catechol structures have been reported, esterification between catechol and $HCrO_4^-$ as well as the coupling between catechol anion and CrO_2^{2+}.[31] However, the esterification mechanism is not popular among researchers, probably because of the difficulties in desorbing the chemically bound Cr(VI). Adsorbents with poor reusability are not ideal as they defeat the purpose of cost-effectiveness in adsorption.

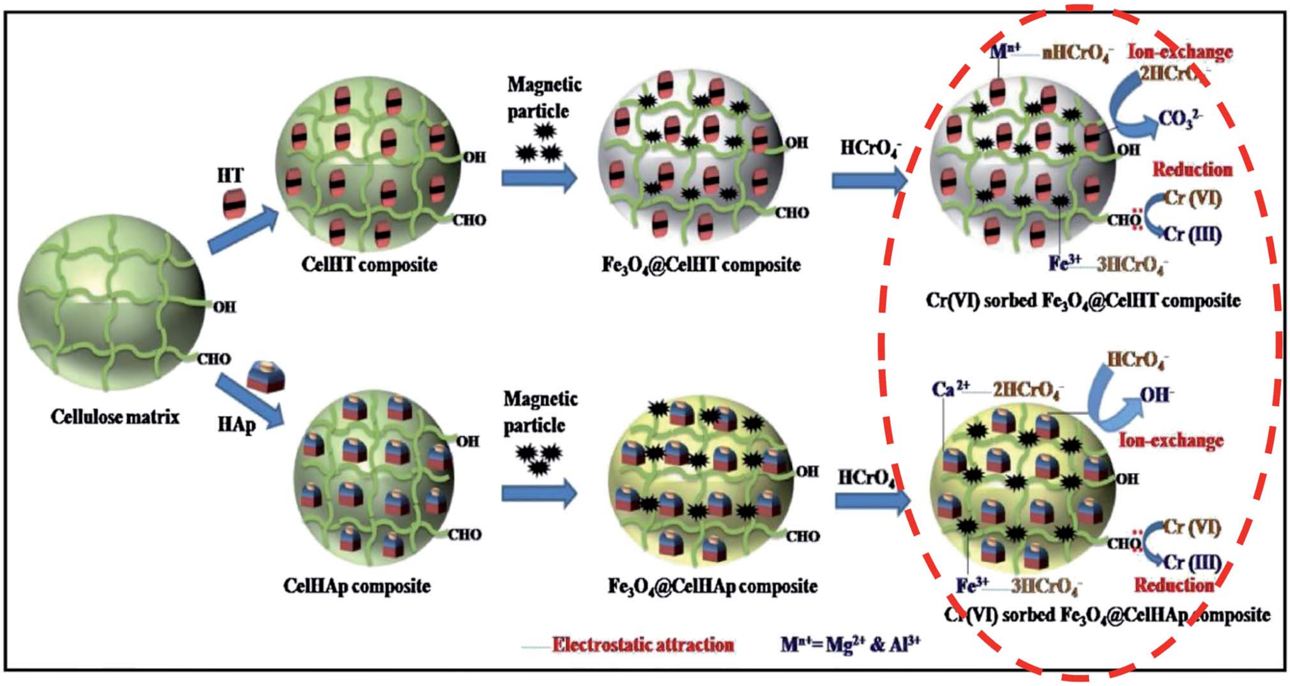

Fig. 3 A possible Cr(VI) sorption mechanism pathway onto magnetic particles imprinted cellulose-based biocomposites. Chromium removal and reduction are occurring at the last step indicated in red, while the other steps show the preparation of biocomposites. Copied from ref. 36, with permission from Elsevier and modified.

4.4. Re-usability of hexavalent chromium adsorbents

Re-usability of various adsorbents for the removal of water pollutants is generally viewed as a good advancement as this can reduce the costs associated with synthesis and purchase of chemicals required for fabrication or modification of some adsorbents. In addition, re-usability prohibits the disposal of adsorbents after a single-use. This supports the green chemistry principles where it is suggested that the production of a large volume of waste should be avoided and proper waste management system needs to be provided.[172] Based on the information presented in Table 1, it is clearly shown that some chromium adsorbents can be re-used after a simple treatment with dilute sodium hydroxide or hydrochloric acid solutions. $NaHCO_3$, NaCl, HCl, HNO_3, distilled water and Na_2CO_3 are other desorbing agents that have been used[3,15,23,89] but NaOH is more popular.[15,23,30,65,158,167] The choice of the desorbing agent used in desorption is based on the nature of the adsorbent surface functional groups, types of bonding interaction and the adsorption mechanism.[148] Araghi *et al.*[148] used sodium hydroxide for chromium desorption as it led to deprotonation of $-NH_3^+$ groups on the adsorbent surface which subsequently resulted in the decrease of electrostatic interactions between these groups and $HCrO_4^-$.[148] In Table 1, the number of repeated use shown indicate the minimum re-usability experiments performed in each case. For example, in the case of polypyrrole magnetic nanocomposite, four adsorption/desorption cycles were conducted.[50] In a different study, the ability to re-use the sandwiched nanocomposite adsorbent synthesized using GO, manganese dioxide nanowires, iron oxide nanoparticles and polypyrrole was reported.[162] As shown in Table 1, the sandwiched nanocomposite possessed the adsorption capacity of more than 282 mg g^{-1} within the first four adsorption/desorption cycles; however, this decreased to 264 mg g^{-1} at the fifth cycle. Other adsorbents which recently showed the capacity to be re-used include AC of *Cornulaca monacantha* stem,[173] ZnO tetrapods as well as AC based hybrid composite,[65] AC modified with micro-sized goethite using a facile impregnation method,[174] crosslinked chitosan[64] and ZnO–TiO_2 doped polyacrylonitrile nano fiber-mat.[175]

3.8. Comparison and contrast of adsorbents based on adsorption capacities for chromium(VI)

Usually, the performance of adsorbents is judged by their adsorption capacity values (Table 2). However, in our opinion, this comparison is not a true reflection or determinant of adsorption performance. This is particularly so because of the complexities involved such as the type of adsorbents, functional groups type and density, and adsorption conditions employed including dosage, pH, and initial concentration. In addition to this, there are other variables such as batch *versus* column adsorption as well as shaking *versus* stirring; all these give different adsorption capacities. Table 2 depicts the different adsorption capacities for Cr(VI) reported by various researchers (selected randomly) and the diverse conditions adopted. Normally the loading (mg g^{-1}) increases with an increase in the initial concentration of the adsorbate, and the generally accepted explanation is that as the adsorbate initial concentration increases the number of moles of adsorbates in solution

Table 1 Re-usability of adsorbents for removal of Cr(VI) from aqueous solutions

Adsorbent	Number of repeated use	Adsorption capacity (mg g^{-1})/performance	Regeneration process	Reference
Polypyrrole magnetic nanocomposite	4	49.7	Desorption with 0.1 mol L^{-1} NaOH and subsequently treated with 2 mol L^{-1} of HCl	43
Sandwiched nanocomposites	4	>282	Desorption is carried out at high pH conditions	162
AC modified with micro-sized goethite	4	Cr removal efficiency of up to 75.1%	Washed with 0.1 M HCl solution	174
AC of *Cornulaca monacantha* stem	5	89% adsorption efficiency	Desorption was carried out with 0.01 mol L^{-1} NaOH	173
ZnO tetrapods and AC based hybrid composite	3	Cr removal efficiency > 90%	Washed with 0.1 mol L^{-1} NaOH, kept at 120 rotations per minute (rpm) for 8 h and dried in vacuum at 60 °C	65
AC modified with micro-sized goethite using a facile impregnation method	4	Cr removal efficiency > 75%	Washed with HCl solutions (0.1 and 1 mol L^{-1})	174
Nanocomposite adsorbent	5	>80% adsorption efficiency	Washed with deionized water and then dried at 100 °C in an oven for 3 h	64
Crosslinked chitosan	5	269	Washed with 1 mol L^{-1} NaOH	176
Tetraethylenepentamine functionalized alginate beads	5	30 (% removal exceeded 80%)	100 mL of NaCl (1 M)/ethanol (98%) solution mixture with continuous shaking at 250 rpm for 1 h at 25 °C	177
Chitosan grafted GO nanocomposite	10	The percentage removal decreased marginally from 96% to 82%	Washed with 1 mol L^{-1} NaOH	178

surpasses the active sites resulting in saturation and maximum adsorption. Using Fig. 4 to illustrate this point, it can be observed that at a higher initial concentration (300 mg L^{-1}) the percentage removal of the pollutant is minimal (20%) while the loading capacity is at maximum. Of the initial 300 mg L^{-1}, only 60 mg L^{-1} was removed (20%) and 240 mg L^{-1} concentration of Cr(VI) was left in solution. Reporting adsorption performance in adsorption capacity somehow hides the truth about the ability of adsorbents. Nonetheless, the adsorption capacity values reported in Table 2 show that researchers are now able to develop adsorbents with very high adsorption capacities, and it is good progress indeed. However, biomass adsorption capacities are

Table 2 Comparison of adsorption capacities from various adsorbents for Cr(VI)

Adsorbents	Adsorption capacity (mg g^{-1})	Initial concentration (mg L^{-1})	Dosage (g L^{-1})	Optimum pH	Reference
Aluminium–lanthanum mixed oxyhydroxide (ALMOH)	49.8	200	2	4.5	15
Chitosan/aluminum–lanthanum mixed oxyhydroxide (CSALMOH)	78.9	200	2	4.5	15
Ionic solid impregnated phosphate chitosan	266.67	1200	4	3	16
PAN–CNT/TiO_2–NH_2	714.27	300	—	2	30
Amberlite XAD (synthetic polymer)	196	50	5	1.5	92
Cr(VI)-IIP anchored on magnetic multi-walled carbon nanotubes	56.1	400	1	3	94
IIP 4-vinyl pyridine and 2-hydroxyethyl methacrylate co-monomers	311.95	1000	0.4	2	101
H_3PO_4 acid-activated (Acticarbone) carbons	186	200	0.6	3	123
KOH-activated activated (Acticarbone) carbons	315	200	0.6	3	123
MS@APTES@PNIPAm	123.8	31	0.2	2.5	147
Mesoporous silica embedded with magnetite nanoparticles	50.51	50	1.4	2	148
Magnetic mesoporous titanium dioxide–graphene oxide core–shell microspheres	117.94	—	—	6.5	156
Resorcinol–melamine–formaldehyde (RMF) anchored on a nanocrystalline cellulose	463	400	0.2	3	157

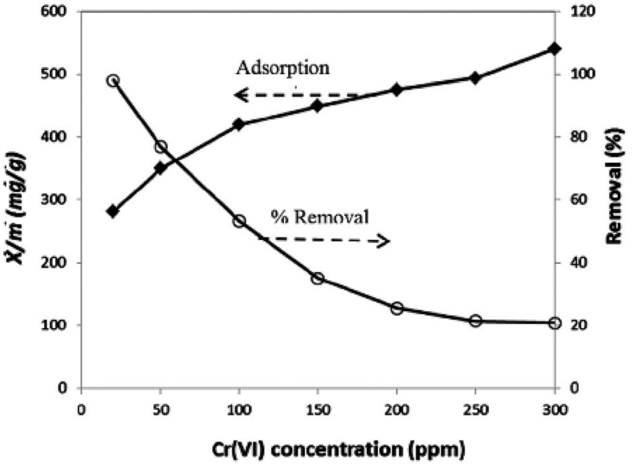

Fig. 4 Demonstration of the effect of initial concentration on percent removal and adsorption capacity.[160]

still low compared to the rest of the adsorbents, and that need improvement if the low-cost effectiveness of adsorbents is to be advanced. More adsorbents of the type adsorbent1@adsorbent2@adsorbent3 need to be developed using biomass and possibly the type of adsorbent1@adsorbent2@adsorbent3@adsorbent4. However, with such complex and expensive chemical usage in adsorbent preparation, would the adsorption method be still advocated as cheap and simple? The authors do not think so.

4.6. Other parameters influencing adsorption capacity

As alluded to in the preceding paragraph, adsorption capacities should never be read alone to infer on the performance of an adsorbent. Several other parameters influence the adsorption capacities. These include the solution pH, equilibration time, temperature of the solution, co-existing ions, and adsorbent dosage concentration. Solution pH affects both the adsorbate and adsorbent chemistry, *i.e.*, the degree of adsorbent functional groups ionization and speciation of chromium.[33] Numerous studies reported on the electrostatic attraction forces between positively charged adsorbent surface groups and anionic Cr(VI) species.[21,23,35,54,65] This is particularly more common because Cr(VI) exists as oxyanions ($HCrO_4^-$, $Cr_2O_7^{2-}$ and CrO_4^{2-}) in aqueous solution. Therefore, conditions conducive for negative–positive attraction will favour the electrostatic attraction. Positively charged adsorbent surface groups are produced by protonation or quaternization. Adsorbents relying on the electrostatic attraction usually give high removal efficiencies at low pH values with adsorption capacities decreasing as the pH is increased due to deprotonation and presence of OH^- ions competing for adsorption sites with Cr(VI) ions. Initial concentration also affects the type of species present and the sorption capabilities. Thus, speciation is affected by both the concentration and pH. The percentage removal decreases with an increase in solute concentration while the adsorption capacity decreases. Adsorption rate also plays a critical role in sorption processes. Hence, the influence of contact time on the adsorption capacity is always studied for all adsorbents to infer on reaction mechanism governing the process. Most adsorbents share a similar trend, where initially, there is a rapid uptake of Cr(VI) due to the abundance of adsorption sites *versus* the fixed moles of Cr(VI) in solution, boundary layer adsorption. The second stage is usually characterized by slow adsorption, termed as the diffusion into internal pores. The third and last stage is the saturation of adsorption sites (equilibrium).[21,23,33,35,54]

Investigation of the effect of co-ions gives an indication of how the prepared adsorbent will perform in real-world samples containing other pollutants that may interfere with Cr(VI) binding to the adsorbent. Cr(VI) behaves as an anion in aqueous media, therefore, investigating its preference by adsorbents using anionic species like F^-, SO_4^{2-}, PO_4^{3-}, Cl^-, and HCO_3^- (ref. 15 and 23) is justifiable. Nonetheless, the influence of mixtures of anions and cations[22,36,56] as well as cations only[62] have been studied. The effect of temperature on the adsorption capacities is studied to infer on the spontaneity of the reaction. Both endothermic[23,36,63,89,158,167,169] and exothermic[15,30] processes for the uptake of Cr(VI) have been reported. The influence of temperature on adsorption is one of the gray areas of the process that are not well researched and explicitly explained. By definition, adsorption is an exothermic process but numerous researchers have justified their endothermic nature findings using scientifically acceptable explanation. With regards to adsorbent dosage concentration, adsorption capacity decreases with increase in sorbent dose. The plausible explanation is that the increase in adsorption performance as the concentration dosage is increased is credited to the increased active adsorption sites as the mass of sorbent is increased. In addition to the aforementioned factors, the presence of surfactants and ionic salts affect the adsorption capacities but there has been very little evidence on their investigation.[179]

4.7. Most recent applications, challenges and future perspectives

Removal of Cr(VI) from aqueous solutions based on adsorption methods is currently the area of intense research. Recent work include removal of Cr(VI) from water samples using *m*-phenylenediamine-modified polypyrrole,[180] sweet lime peel powder,[111] chitosan-based hydrogel,[181] nanocarbon bridged nano magnetite network,[182] magnetic biochar composite,[183] carbon spheres (magnetic ceramsite coated by functionalized nano carbon spheres[184] and hollow carbon spheres[185]), modified sponge iron particles[186] and metal–organic framework.[187] Recent work has provided evidence that the modified and functionalized adsorbents perform better than their natural forms. For illustration, the equilibrium adsorption capacity achieved for Cr(VI) in water using magnetic biochar was 8.35 mg g^{-1},[183] whereas, the amino-functionalized magnetic biochar yielded the maximum adsorption capacity of 142.86 mg g^{-1}.[188]

Some adsorbents recently reported in the literature are waste materials which are regarded as low-cost sorbents. Typical examples include eggshell powder,[189] orange peels,[190] coffee ground and mixed waste tea,[191–193] human hair waste[194] as well as rock wool.[4] The application of these adsorbents in water purification is advantageous in green chemistry perspectives as these are prevented from invading the environment. The current concern with their usage in Cr(VI) removal, which can be investigated in the future arise from their application in deionized water. Therefore, the applicability of the number of reported adsorbents in real samples such as industrial wastewater, seawater, where high concentrations of chromium are expected is not well understood. Another challenge is the inability to re-use some adsorbents. For example, Kera *et al.*[180] demonstrated that the removal of Cr(VI) using *m*-phenylenediamine-modified polypyrrole adsorbent decreased by approximately 30% after the third adsorption/desorption cycle. This implies that there is a chance that the highly contaminated adsorbent used for Cr(VI) removal from water could be disposed into the environment. Regarding the reusability of adsorbents, Samuel *et al.*[64] observed a significant decrease in the adsorption/desorption of Cr(VI) after each cycle using a nanocomposite adsorbent material synthesized from chitosan, GO and metal–organic framework. Even though these adsorbents could be useful in water decontamination, their single-use might result in their excessive disposal into the environment. The stability of many adsorbents reported in the literature for Cr(VI) adsorption is not known. The stability of adsorbents stored for an extended period of time has only been investigated in a few studies. For example, Sharma *et al.*[65] investigated the stability of ZnO-tetrapods and AC based hybrid composite by performing adsorption after six months of adsorbent synthesis. The removal efficiency was used as a measure of stability.

4.8. Concluding remarks

The aim of this article was to review some of the major adsorbents used for Cr(VI) confiscation from aqueous solution to provide a one-stop resource material for researchers working on the adsorptive removal of Cr(VI). The classification of adsorbents, characteristics, and their development history together with the toxicity of chromium, its sources, mechanism of removal and recent trends in adsorbent synthesis and preparation were discussed at length. The advancement in the interpretation of the Cr(VI) removal mechanism was outlined, and the main challenge identified was accounting for the fate of the as-reduced Cr(III). Irrespective of the type of adsorbent used, reporting only on adsorption of Cr(VI) through electrostatic attractions is not enough when it is known that Cr(VI) is a strong oxidant susceptible to undergo transformation to Cr(III) upon accepting electrons. Heteroatoms like O, N, and S responsible for the donation of electrons are present in almost every adsorbent. Hence, direct or indirect reduction of Cr(VI) to Cr(III) during adsorption cannot be ruled out. Disproving the presence or absence of Cr(III) in solution or adsorbent surface following Cr(VI) uptake is paramount. The qualitative determination of Cr(III) presence by the greenish-colour of adsorbents after adsorption is not enough proof of reduction on its own. It needs to be supplemented by analytical instruments. Characterization of the adsorbent surface by XPS after adsorption and analysis of solution with atomic absorption spectroscopy does indicate the presence or lack of Cr(III) after adsorption. The removal mechanism is also affected by surface chemistry and physical properties of adsorbents. The characteristics of high surface area, availability, porosity, and cost-effectiveness are considered when developing adsorbents for pollutant removal. AC, GO, nanoparticle, and silica are known for their high surface area values, while biomass exhibit low surface area but abundant functional groups. Functionalization and merging of adsorbents into composite materials produce superior properties. The recent literature shows that most of these adsorbents are no longer used in their pristine form, but several modifications are carried out. Functionalization could be achieved by cross-linking and/or grafting. Better performances have been reported where there were three levels of modifications in an adsorbent1@adsorbent2@adsorbent3 system of layers have been used. Some of these layers not only consisted of ligands but also composite materials from different adsorbents, *e.g.*, silica@nanoparticle@polymer. With such modifications, good (78.90, 123, 196 and 198 mg g^{-1}) and excellent (315 and 714.27 mg g^{-1}) adsorption capacities have been achieved. In the case of PAN@CNT@TiO_2@NH_2 composite (714.27 mg g^{-1}) the high surface area property of TiO_2 was complemented by the inclusion of NH_2 groups for Cr(VI) adsorption. It should be taken into cognizance that adsorption capacity values need to be viewed with other parameters influencing adsorption. For instance, some of these adsorbents reached equilibrium after 14 h, while others only needed 30 min. Longer equilibration times could not be ideal for the industrial application of adsorbents. Also, most experiments giving the high values of adsorption capacities were conducted with deionized water. But, it was evident that for much more improved adsorption performance, modification of the structure and functional groups of adsorbents should be performed concurrently. This was demonstrated in the synthesis of hierarchical structure that exhibited high adsorption capacities (463 mg g^{-1}). Adsorbents representing triple or double grafting of the type adsorbent1@adsorbent2@adsorbent3@adsorbent4 composite could also be the future, but adsorption is advocated as a simple and low-cost method. The cost could be offset by the performance (714.27 mg g^{-1}) as demonstrated in the PAN@CNT@TiO_2@NH_2 composite. Therefore, complex adsorbent preparation should be balanced by their superior adsorption performances; otherwise, it will be fruitless to have a complex adsorbent with poor adsorption capacity.

Conflicts of interest

There are no conflicts to declare.

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