Polymeric sorbents for removal of Cr(VI) from environmental samples*

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Abstract: Chromium (Cr) is an important raw material in some chemical industries including paint, pigments, textiles, leather tanning, steel fabrication, electroplating, cement preservation, and canning industries. Once in the environment, Cr exists in various oxidation states depending on pH and concentration. Trivalent [Cr(III)] and hexavalent [Cr(VI)] forms are the most common with Cr(VI) being the most toxic to biota. The review discusses various types of polymeric sorbents that have been prepared for the extraction of Cr(VI) from environmental samples, mostly aqueous samples. Sorbents are categorized into biosorbents, hybrid sorbents, synthetic polymeric, and modified natural polymeric sorbents. Most of the emphasis will be on the advantages and disadvantages of different synthetic polymeric sorbents. Important parameters that define the performance of the sorbents, that is, binding capacity, equilibration time, optimum sample pH, and selectivity, are compared.

Keywords: adsorption; adsorption capacity; materials chemistry; chromium VI; selectivity; sorbents; waste; wastewater.

INTRODUCTION

For the past few years, research has been focused on developing methods for selective removal of Cr(VI) from environmental samples and drinking water. Cr(VI) is more carcinogenic and mutagenic to living organisms than Cr(III) with toxicity effects related to its chemistry [1]. The World Health Organization (WHO) has set Cr(VI) maximum permissible level of 50 µg/L in wastewater [2–4]. On the other hand, Cr(III) occurs naturally in the environment and is required for mammalian metabolism actions. Stringent laws on Cr(VI) effluents have provoked commendable interest in research related to its extraction, and noticeable success has been achieved as is shown recently with adsorption methods [5–10]. Cr(VI) is dominant in oxidized environments, making it more bioavailable, mobile, and a health risk [11]. Hence, its removal from wastewater before being discharged into the environment is vital. According to Eh–pH diagrams, the species dominant at low pH and oxic conditions are $HCrO_4^-$, CrO_4^{2-}, and $Cr_2O_7^{2-}$. All three have different geometries, and their speciation will depend on the pH and concentration of Cr [12]. Therefore, the method used for Cr(VI) removal must try to address the noted variations. Several techniques (ion exchange, chemical precipitation, filtration, membrane technologies, coagulation, electrodepositing, adsorption, etc. [5]) have been used for Cr(VI) removal but the emphasis here is on adsorption methods. Research interest has shifted to adsorption methods because they offer high efficiency and selectivity, are easy to handle, reversible, and cost-effective [6,13].

Synthetic polymers and biosorbents are mostly used as sorbents during adsorption studies. Removal of Cr(VI) by adsorption onto polymers has been a popular choice in the developed world [14]. Nonetheless, the design of metal-chelating polymers has to be pinpointed in order to produce polymers with significant specificity and selectivity for the removal of metal ions [15,16]. Criteria such as the nature and location of functional groups in a sorbent, sorbent capacity, selectivity, and the rate of complexation of metal ions are imperative [15,16]. The review attempts to critique the nature and chemistry of functional groups that have been utilized on sorbents and their influence on adsorption capacity, rebinding time, sample pH, and selectivity of sorbents. The nature and location of adsorption sites are important for any sorbent to function properly for a specific metal ion. It is desirable that the functional groups be at the surface or near the proximity of the surface of any sorbent to influence faster rebinding kinetics. The porous nature of the sorbent determines the location of chelating groups. More porous materials tend to have easily accessible sites that are near or at the proximity of the surface. Cr(VI) is a hard acid, therefore one would expect it to interact more strongly with hard bases such as NH_3, CH_3COO^-, or CO_3^{2-}. Therefore, it is not surprising that most sorbents used for Cr(VI) extraction either contain amino and/or carboxyl groups. A literature survey reveals that most successful ligands used for Cr(VI) adsorption are those containing tertiary amine and quaternary amine [8,17–19].

Cr(VI) in an aqueous environment exists as an oxyanion, and that is the reason why ligands carrying a positive charge, either due to protonation or quaternization, have been successfully used because electrostatic attractions are favored. Ligands used should be flexible enough to accommodate the different geometries for complete extraction of Cr(VI). Although synthetic polymers could be arguably more expensive than natural or modified natural biosorbents, they could offer better modification of the functional groups during synthesis, leading to better performance in Cr(VI) extraction. The scope of biosorbents, which includes chitosan, cellulose etc., is wide, and recently, Miretzky and Cirelli [20] reviewed the application of raw and modified lignocellulosic materials, for the removal of Cr(VI) and Cr(III) from aqueous solution. However, some biosorbents will be mentioned but only in comparison with optimum parameters for Cr(VI) adsorption and future direction to synthetic polymers. The following parameters, extraction time, loading capacity, and selectivity and sample pH are compared.

OVERVIEW OF POLYMERIC SORBENTS

Polymers are large molecules produced by recombination of several monomer units. Depending on the reaction conditions used during preparation, polymers can either be in liquid or solid form. It is only in solid form where polymers can be used for adsorption studies. To achieve solid form, polymers are either cross-linked with an appropriate cross-linking monomer or attached to solid supports. The support can be an inorganic substrate as in Fe_3O_4 [7,9,12,17,21–23] and SiO_2 [23], humic acids [24], or a natural material like chitosan [5,25,26] or wood saw dust [27]. Particularly, synthetic polymers offer numerous advantages, e.g., during production one may control properties like size distribution, porosity, hydrophobicity, size of polymer chain, and particle size, etc., as well as after preparation polymers can still be modified by insertion of specific ligands into the polymer backbone structure [6]. The advantageous properties of synthetic polymers are linked to the type of monomer and preparation conditions used. Therefore, the choice of monomers is crucial and it is also governed by the type of interactions and the nature of pollutants to be extracted. The pollutant can be a neutral molecule, cationic or anionic. Cr(VI) exists as anionic species in aqueous media. Some monomers may be expensive, but polymeric sorbents are very stable and can be re-used for a number of times, which then offset the expense.

Introduction of hydrophilicity in the polymer is sometimes necessary because hydrophobic polymer sorbents show poor adsorption capacity in aqueous media due to poor wettability of the surface [28]. A hydrophilic *N*-vinylimidazole comonomer was used for extraction of Cr(VI) from aqueous media [6]. The incorporation of hydrophilic moieties in the polymer was to improve Cr(VI) adsorption but 108 mg/g adsorption capacity [6] obtained did not show major advantages in using hydrophilic

monomer when these results are compared to those in Table 1 from hydrophobic polymers. The reason could be that the mechanism of removal is electrostatic attraction and is less affected by aqueous environments compared to say weak van der Waals forces. Therefore, the choice of using a hydrophilic monomer is maybe not justified particularly if you consider the initial Cr(VI) concentration used of 3000 mg/L. In the authors' defense, only about 1 % adsorption capacity was achieved when adsorption studies were conducted with the same polymer (acrylate) but without vinylimidazole ligand. So, the imidazole functionality was responsible for the adsorption capacity demonstrated, not the acrylate functionality. Low sorption capacity (29.67 mg/g) was also achieved with poly(methylacrylate) polymer sorbent [29], suggesting that acrylate is not an apt ligand for Cr(VI) adsorption. In contrast, high sorption capacity (162.9 mg/g) was reported with polyglycidyl methacrylate polymers [22]. The only concern with those results is that the authors described the Cr(VI) removal mechanism taking place as anion exchange due to protonation of amino groups at low acidic conditions. That cannot be right considering there were no amino-bearing substrates used in their polymer preparation. Unless there was an oversight and amino reagent was omitted under experimental, then that would clarify that the higher adsorption is actually due to amine moieties not acrylate.

Anion-exchange resins containing various alkyl, benzyl chloride, and halo ketone substituents have been reported [5,8,18,30]. Strong base anion exchangers with pyridine moieties displayed high selectivity for Cr(VI), and these were presented to be the foundation for selective removal of Cr(VI) [8]. For anion exchangers, two factors controlling adsorption capacity are the nature of substituent on the quaternary ammonium atoms and the ionic form of the base [8]. The mechanism of Cr(VI) removal with quaternized materials is electrostatic attraction and ion exchange. The presence of bulky substituents on the quaternary nitrogen might present steric hindrance properties leading to lower adsorption capacity. Therefore, one might expect that use of smaller halogenated molecules is the way forward. However, because of the size of chromate ions, if small molecules are used it leads to a problem of having smaller cavities where chromate ions will have difficulties to fit in. On the other hand, bulky molecules open up the spaces between polymers so that chromate can fit in but only for steric hindrance. Hence, a compromise between bulky and small halogenated molecules to be used in quaternization has to be found.

METAL ADSORBENTS

Removal of Cr(VI) by biosorbents

Selected examples of biosorbents used for Cr(VI) removal are reviewed for the purpose of comparison with synthetic polymeric sorbents. Equilibrium studies were conducted for the sorption of Cr(VI) onto Kraft lignin as an adsorbent [31]. The results fitted best the Redlich–Peterson isotherm. Optimal adsorption capacity was ca. 0.19 mmol/g (~40 mg/g) [31]. Coconut coir and char have also been used for hexavalent Cr removal from wastewaters [32]. Sorption capacity reported [32], 70.4 mg/g, from an initial solution concentration of 500 mg/L was higher than 27 mg/g capacity obtained by Gonzalez et al. [33] also from coconut coir. Osage orange (*Maclura pomifera*) was explored as an adsorbent for Cr(VI) removal [34]. The observed maximum biosorption capacity by Langmuir sorption model at pH 2 for *M. pomifera* pulp and peel was 198 and 118 mg/g, respectively. The equilibration time was 120 min. Elsewhere, citric-acid-treated walnut shell (WNS) (*Juglans regia*) was used as an adsorbent for Cr(VI) removal from aqueous solutions [35]. Optimal conditions obtained were 129 mg/g adsorption capacity, pH 3, and 120 min equilibration time. Biosorbent results mentioned in this paragraph are from the past two years (2011 and 2012). It can be observed that the sorption capacities and equilibration times mentioned are comparable with some of the synthetic polymer sorbent in Table 1. Synthetic polymers offer better fine-tuning options than biosorbents, and hence, their combination with biosorbents might produce sorbents with superior selectivity, high loading capacity, and shortest equilibration time.

Table 1

Sorbent	Reactive functional units	Cr(VI) determination	Mechanism	Binding capacity mg/g	Initial concentration mg/L	Equilibration time, min	Initial pH	Selectivity	References
Synthetic polymers and organic-inorganic hybrid materials									
Polyethyleneglycol methacrylate-co-vinyl imidazole copolymer (PEGMA-co-VI)	Imidazole and acrylate	UV/Vis	Electrostatic attraction	108.7	3000	120	3	Not tested*	[6]
Magnetic poly-(MA-DVB) graft dendrimer microspheres	Dendrimer			231.8	30	12	3	Not tested	[37]
The m-poly(DVB-VIM) microbeads	Imidazole	UV/Vis	Electrostatic attraction	35.41–101.3	1000	300	2	Not tested	[59]
Polypyrrole-polyaniline (PPy-PANI) nanofibers	Amino groups	UV/Vis	Ion exchange	227	100	30	2	Not tested	[56]
Bamboo-like polypyrrole (PPy) nanotubes	Pyrrole	UV/Vis	Electrostatic attraction	1972	420	1400	3	Not tested	[48]
Polyglycidyl methacrylate graft copolymer (PGMA)	Methacrylate	UV/Vis	Ion exchange	132.5	20	30	4	Not tested	[22]
Iron oxide modified polyglycidyl methacrylate graft copolymer (PGMA) hybrid adsorbent (PGMAFe)	Methacrylate	UV/Vis	Ion exchange	162.9	20	30	4	Not tested	[22]
Activated carbon derived from acrylonitrile-divinylbenzene	Hydroxyl	AAS and UV/Vis	Electrostatic attraction	101.2	30	30	2	Not tested	[61]
Amino-functionalized nano-magnetic polymer adsorbents (NH_2-NMPs)	Amino groups	Standard APHA method	Ion exchange	136.89–307	50–100	-	2	High***	[62]
Poly(ortho-phenylenediamine) fluffy microspheres	Amino groups	AAS	Ion exchange	98.23	50	90	4	Not tested	[73]
Magnetite-plyethylenimine montmorilonite	Amino groups	UV/Vis	Electrostatic attraction	8.77	24	120	6	Not tested	[60]
Ferromagnetic poly(acrylic acid acrylonitrile) P(AA-AN) R2	Acrylic acid acrylonitrile	UV/Vis	Electrostatic attraction	951.4	10	180	5.1	Not tested	[23]
Amino-functionalised mesoporous silica	Amino groups	AAS	ctrostatic attract	2.28 nmol/g	100	60	4.5–6.1	Not tested	[79]
Bio-functional magnetic beads	Amino groups	AAS and UV/Vis	Ion exchange	6.73	40	480	1	Not tested	[17]
Magnetic poly(GMA–EGDMA)	Imine	UV/Vis	Electrostatic attraction	137.7	200	120	2	Not tested	[7]
Functionalized pyridine copolymer with amide groups	Quaternized ammonium aoms	AAS	Ion exchange	82.46	116	120	3	High	[18]
Poly(methylacrylate) functionalized guar gum	Acrylate	UV/Vis	Electrostatic attraction	29.67	400	1440	1	Not tested	[29]

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Table 1 (*Continued*)

Sorbent	Reactive functional units	Cr(VI) determination	Mechanism	Binding capacity mg/g	Initial concentration mg/L	Equilibration time, min	Initial pH	Selectivity	References
Ethylenediamine (EDA)-functionalized magnetic polymers (EDA-MPs-2)	Amino groups	UV/Vis	Electrostatic attraction	32.15	100	60	2.5	Not tested	[21] #
Ethylenediamine (EDA)-functionalized magnetic polymers (EDA-MPs-4)	Amino groups	UV/Vis	Electrostatic attraction	36.63	100	60	2.5	Not tested	[21] #
Ethylenediamine (EDA)-functionalized magnetic polymers (EDA-MPs-6)	Amino groups	UV/Vis	Electrostatic attraction	49.5	120	60	2.5	Not tested	[21] #
Ethylenediamine (EDA)-functionalized magnetic polymers (EDA-MPs-8)	Amino groups	UV/Vis	Electrostatic attraction	60.98	140	60	2.5	Not tested	[21] #
Ethylenediamine (EDA)-functionalized magnetic polymers (EDA-MPs-10)	Amino groups	UV/Vis	Electrostatic attraction	61.35	140	60	2.5	Not tested	[21] #
Quaternized poly(4-vinylpyridine)	Quaternary amino	AAS	Ion exchange	33	138	1440	3	High	[8]
Poly(aniline-1,8-diaminonaphthalene) (PANDAN)	Amino groups	AAS	Electrostatic attraction	154.2	400	200	4	Moderate	[38]
Imprinted 4-Vinylpyridine/Methacrylic acid polymer	Vinylpyridine and acrylic acid	IC-HPLC UV/vis	Electrostatic attraction	37.58	60	120	3	Moderate	[19]
Non-imprinted 4-Vinylpyridine/Methacrlic acid polymer	Vinylpyridine and acrylic acid	IC-HPLC UV/Vis	Electrostatic attraction	25.44	60	120	3	Low	[19]
Imprinted 4-VP/HEMA	Vinylpyridine	UV/Vis	Electrostatic attraction	(3.31)*	200	50	4	High**	[80]
Poly [3-(acryloylamino) propyl] trimethylammonium chloride, P(ClAPTA)	Tertiary ammonium	AAS	Electrostatic attraction	164	30		9		[36]
Poly (ar-vinyl benzyl) trimethylammonium chloride, P(ClVBTA)	Tertiary ammonium	AAS	Electrostatic attraction	152	30		9		[36]
Poly[2-(acryloyloxy)ethyl] trimethylammonium methylsulfate, P(SAETA)	Tertiary ammonium	AAS	Electrostatic attraction	90	30		9		[36]
Polyethylenimine - $Fe_2O_3@Fe_3O_4$ magnetic nanoparticle	Imine	UV/Vis	Ion exchange	83.33	100	30	3	High	[81]
Polypyrrole/Fe_3O_4 magnetic nanocomposite	Pyrrole	UV/Vis	Electrostatic attraction	169.4	200	30	2	Not tested	[9]
Polyaniline/humic acid composite	Amino groups	AAS	Ion exchange	150	15	120	5	High	[24]

Table 1 (*Continued*)

Sorbent	Reactive functional units	Cr(VI) determination	Mechanism	Binding capacity mg/g	Initial concentration mg/L	Equilibration time, min	Initial pH	Selectivity	References
Based on natural polymers									
Crosslinked chitosan	Hydroxyl and amine	UV/Vis	Electrostatic attraction	84.19	30	120	3	Not tested	[13]
Thiocarbamoyl chitosan (TC–Chitosan)				434.8	1000	240	2	Not tested	[82]
Polyethylene and agave fibers coated with chitosan			Electrostatic attraction	200	1000	20	4	Not tested	[83]
Short chain polyaniline synthesized on jute fiber	Aniline	UV/vis and AAS		62.9	100	360	3	Not tested	[10]
Polyaniline–jute fiber				4.66	20	-	3	Not tested	[45]
Chitosan	Amine and hydroxyl	UV/Vis	Electrostatic attraction	102	100	-	3	Not tested	[26]
Immobilized chitosan as biosorbent	Hydroxyl and amine	AAS	Electrostatic attraction	0.46*	1 mmol/L	450	4	Not tested	[25]
Chitosan coated with poly 3-methyl thiophene polymer	Thiophene	UV/Vis	Ion exchange	127.62	200	100	2	Not tested	[5]
Inorganic sorbents									
Powdered activated carbon	Activated carbon	UV/Vis	surface adsorption	79.2	500	26	2.32	Not tested	[84]
Organic–inorganic hybrid of chitosan/organoclay bionanocomposites				357.14	100	180	3	Not tested	[85]
Synthesized CeO_2 nanoparticles				1.88	0.6	-	7	Not tested	[86]
Synthesized CeO_2 nanoparticles				83.33	37.5	-	7	Not tested	[86]
Synthesized CeO_2 nanoparticles				121.95	80	-	7	Not tested	[86]
Polymeric Fe/Zr pillared montmorillonite				22.35	50	120	3	Low	[76]

Table 1 (*Continued*)

Sorbent	Reactive functional units	Cr(VI) determination	Mechanism	Binding capacity mg/g	Initial concentration mg/L	Equilibration time, min	Initial pH	Selectivity	References
Biosorbents									
Alligator weed	Hydroxyl, amino, carboxyl	UV/Vis	Electrostatic attraction	82.57	360	-	1	Not tested	[87]
Polyaniline/kapok fiber				50.05	100	300	4.5	Not tested	[39]
Modified corn stalk				93.41	300	210	4.91	Not tested	[88]
Nanoscale zerovalent iron (NZVI) supported on the pillared bentonite	Bentonite	UV/Vis	Reduction adsorption	4.2	200	120	5.6	Not tested	[89]
Coconut coir biosorbent	Hydroxyl	ICP-OES and UV/Vis	Electrostatic attraction	26.8	200	20	2	Not tested	[33]
Raw green alga Oedogonium hatei				31	100	120	2	Not tested	[90]
Acid-treated green alga Oedogonium hatei				35.2	100	120	2	Not tested	[90]
Pre-boiled sunflower stem	Hydroxyl carboxyl	AAS	Electrostatic attraction	4.9	50	180	2	Not tested	[74]
Formaldehyde-treated sunflower stem	Hydroxyl carboxyl	AAS	Electrostatic attraction	3.6	50	180	2	Not tested	[74]
Polypyrrole/wood sawdust	Pyrrole	UV/Vis	Ion exchange	3.4	100	15	5	Not tested	[27]
Polyethylenimine-modified fungal biomass	Imine	ICP-OES and UV/Vis	Ion exchange	279.2	3.85 mmol/L	360	4.6	Not tested	[91]
Spent cyanobacterial biomass from a hydrogen fermentor				39.2	50	-	3	Not tested	[92]
Mercaptosilane functionalized sepiolites (acid-activated)				7.73	100	1440	4.7	Not tested	[93]
Mercaptosilane functionalized sepiolites (natural)				2.68	100	1440	2.5	Not tested	[93]

* the value is in mmol g^{-1}. Authors did not name the source of Cr(VI) ions used to help with conversion
** selectivity Ni(II) and Cr(III) were used not anions
*** Only tested against Cu(II)
#The number after EDA-MPs is the different amount of glycidylmethacrylate (GMA) used (2, 4, 6, 8, 10 mL) which translates to level of crosslinking

Removal of Cr(VI) by synthetic polymeric sorbents

There is a wide range of synthetic polymeric sorbents available that can be used for Cr(VI) removal. However, some of the polymers can be very unselective towards Cr(VI) but nonetheless they are still effective. Polymer sorbents are prepared by various methods, viz., free radical polymerization [19,36], gamma radiation polymerization [23], graft polymerization [29,37], oxidation polymerization [9,10,38], dispersion/suspension polymerization [6–8,21,17,18,39,40], atom transfer radical polymerization [22], etc. The method of preparation depends on the available starting materials and the goal of the researcher. Besides the use of sophisticated polymers, simple polymers like polyvinylpyridine [8], polypyrrole (PPy) [9], polyaniline (PAN) [41], etc. have also been used for removal of Cr(VI).

The aforementioned polymers make an interesting group for the removal of Cr(VI) because of their functionality, particularly amine groups and anionic nature of Cr(VI). For an example, PAN is one of the most extensively studied conducting polymers because it is easy to synthesize and possesses high environmental stability [39]. The amine functionalities on polymers make them partially positive under acidic conditions, thereby creating interaction between cationic moieties and the negatively charged chromate ion. PAN has shown promising applications for metal removal not only Cr but for other metals as well, Hg(II) [42] and arsenate [43]. For Cr removal, PAN has been used by several authors [10,41,44]. However, recently the focus has been on incorporating renewable resources with synthetic polymers to give a new dimension to normal polymers. The combination of renewable resources and synthetic polymers capitalizes on the biocompatibility and environmental friendliness of the renewable materials as well as the physical and mechanical properties of the synthetic components [39]. Similarly, PAN/jute fiber composite adsorbent for Cr(VI) removal was developed [45]. Elsewhere, Zheng et al. [39] replaced jute fiber with kapok fiber to develop a PAN/kapok fiber composite adsorbent for Cr(VI). The adsorption of Cr(VI) on kapok-fiber-based PAN (50.05 mg/g) was much higher than that of jute-fiber-based PAN (4.66 mg/g). The authors attributed the higher adsorption capacity to the chemical and physical nature of the kapok fiber [39]. Kapok fiber, which is made from cellulose, xylan, and lignin [46], has a homogeneous hollow tube shape which grants a direct growth orientation of PAN as well as accelerating the adsorption rate of analyte [39]. Also, polymeric sorbents bearing a vinyl triazole have been used for Cr(VI) removal [47].

Another interesting development has been the combination of polymers and nanotubes for enhanced removal of metal ions. Bamboo-like PPy nanotubes were prepared and applied for Cr(VI) removal from aqueous media [48]. Higher adsorption capacity (1972 mg/g) was observed when bamboo-like PPy nanotubes were compared to traditional PPy nanotubes [48]. The reasons for the noted higher performance were not discussed in the paper, but instead the focus was more on the preparation method. However, the authors predict that the higher sorption capacity was partly due to PPy and the morphology of bamboo-like nanotubes. PPy has a similar structure as 1.5-diphenylcarbazide, a reagent specific for Cr(VI). The PPy structure could rather be very interesting, noting that an adsorption capacity of 169.4 mg/g was observed when PPy was coated on magnetite nanoparticles [9]. The only difference is that in magnetite, only half the concentration of Cr(VI) was used and the equilibration time was short (30 min). One of the shortcomings with the materials so far could be the longer equilibration time needed (about a day), which could be justified by the larger adsorption capacity (~1972 mg/g) demonstrated by materials. Nevertheless, these materials could prove to be very useful in the future since the adsorption capacity is the primary parameter for an adsorbent. Particularly for highly polluted waters, such a sorbent could be very useful. That is, the use of modified nanomaterials could be an area where future research is concentrated on, as far as a metal pollutant adsorption is concerned.
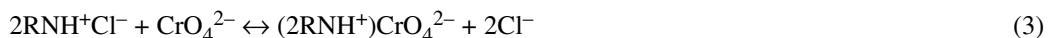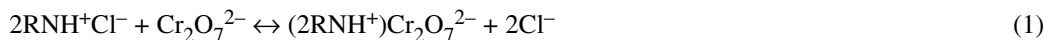
Natural polymeric sorbents

Natural polymeric sorbents are an intriguing group of biosorbents for heavy metal ion removal from environmental samples. Earlier research was on the use of natural polymers as they are but recently researchers have been looking at ways of improving the performance through functionalization. As mentioned in the introduction, natural polymers form a wide range of polymers. However, the most

widely used for metal uptake is chitosan. Chitosan, the product of alkaline partial deacetylation of chitin, is a cationic aminopolysaccharide copolymer of glucosamine and *N*-acetylglucosamine [49]. One of the most abundant biopolymers in nature, chitin originates from crustacean shells like crabs and prawns [49,50]. Its wide use in metal removal is attributed to the greater density of functional groups, ease of handling, economical benefits, and easy functionalization [51–53]. Several reviews have been written on the use of functionalized chitosan for the removal of various metal pollutants from waste-waters [25,54,55].

Cr(VI) ADSORPTION MECHANISM

Few adsorption mechanisms for Cr(VI) have been proposed. These are electrostatic attraction, ion exchange, physico-chemical adsorption, and reduction of Cr(VI) to Cr(III). Some of these mechanisms do take place simultaneously. Electrostatic attraction occurs as a result of attraction between anionic Cr(VI) species to positively charged ligand molecules. The charge on ligand molecules could either be due to quaternization or protonation. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) are used to adjust pH during Cr(VI) adsorption studies. Mechanism of adsorption when protonation of amino groups is due to HCl acid addition, is usually ion exchange between the doped Cl^- ion and Cr(VI) species [56]. The exchange is represented by the following equations [30]:

$$2RNH^+Cl^- + Cr_2O_7^{2-} \leftrightarrow (2RNH^+)Cr_2O_7^{2-} + 2Cl^- \tag{1}$$

$$RNH^+Cl^- + HCrO_4^- \leftrightarrow RNH^+HCrO_4^- + Cl^- \tag{2}$$

$$2RNH^+Cl^- + CrO_4^{2-} \leftrightarrow (2RNH^+)CrO_4^{2-} + 2Cl^- \tag{3}$$

Quaternized materials also undergo ion exchange mechanism [5,8,18,19,30] and possess a permanent positive charge whilst protonation is affected by pH. Quaternization and protonation methods are specific for Cr(VI) adsorption because Cr(III), even if it is present at low pH, gets repelled by the adsorbent [10,29]. The presence of electron-rich moieties in the polymer sorbent might initiate reduction of Cr(VI) to Cr(III) leading to inaccuracy in determining Cr(VI) concentration [20,57,58]. Therefore, it is important to analyze total Cr using either inductively coupled plasma-optical emission spectroscopy (ICP-OES) or atomic absorption spectroscopy (AAS). The Cr(III) so formed is released to aqueous solution or complexed by adjacent functional groups in the polymer [20]. Noticeably, most researchers [5–7,9,21,22,56,59,60] have overlooked the possibility of reduction in determining Cr(VI) when using the diphenylcarbazide method as well as using certified reference materials to validate their methods. Nevertheless, some have determined both Cr(VI) and total Cr using diphenylcarbazide method and AAS, respectively [10,17,61].

The issue of reduction is much more relevant to determine particularly if real world samples are analyzed. If Cr(VI) in real samples is quantified as less than it is supposed to be, due to reduction, then that parody could lead to severe health risk problem as researchers will fail to alert communities of contamination. Nonetheless, few researchers tested their sorbents on real environmental samples [10,19,29,33]. Although some researchers tested selectivity for Cr(VI) using other competing anions [8,18,24,56,61], a substantial number did not test selectivity nor apply in real samples [5–7,9,17,21–23,25,26,36,40]. Therefore, this is one area of concern. Future researchers should demonstrate that prepared polymers are still selectivity for Cr(VI) even when applied to real samples.

As pointed out previously, Cr speciation depends on the pH and Cr concentration. Table 1 reveals that maximum adsorption was achieved at pH < 5, and this is not surprising considering that various Cr(VI) species exist at low pH. Carboxylic acid (–COOH) and amino (–NH₂) functional groups remain protonated at low pH, with amino moieties carrying an extra positive charge. Imidazole has pK_a of about 6, and maximum adsorption capacity was achieved between pH 2 and 5 when a polymer with vinyl-imidazole functionalities was used [6]. It can be said that the polymer was protonated at pH < pK_a values, hence attraction of the anionic Cr(VI) species to the positively charged amino sites [9,62]. One

other advantage of doing adsorption at low pH is that it eliminates the potential for adsorption of cationic metal species due to repulsion with protonated sites [62]. Some competitors that should be tested against Cr(VI) are the anionic species including sulphates (SO_4^{2-}), phosphates (PO_4^{3-}), fluorides (F^-), nitrates (NO_3^-), etc. Surprisingly, most researchers have opted to miss that point as one can see by glancing at Table 1 that selectivity tests were not done for most of polymers listed. It then provokes a question as to whether the synthesized polymers were specific for Cr(VI) or just the same as general-purpose sorbents like activated carbon, chitosan, and lignocellulose.

CHARACTERIZATION OF SORBENTS

Characterization of the sorbents is very important because it helps one to understand the type of functional groups on the surfaces (chemistry of the sorbent) and also the nature of interaction with Cr(VI). It also facilitates the understanding of morphology and to some extent the composition of the sorbent. Unfortunately, no such single technique can do all of the above. A number of techniques are used and are briefly discussed.

Techniques for evaluation of the sorbent–Cr(VI) interaction

For synthetic polymers such as ion-imprinted polymers (IIPs), one needs to evaluate the template [Cr(VI)] and ligand (monomer) interaction in solution and in the final product. IIP recognition sites are generally a direct function of template–monomer interaction. Theoretical predictions have been developed in order to understand the template–ligand interaction strength. The list includes predicting the ligand-metal ion or ligand-receptor binding constants [63] and factorization of the energetic contributions to binding, but mostly for other chemicals not Cr(VI) [64–66]. Besides the theoretical attempts, there are techniques that can help to understand the interaction between the monomer and template, like spectroscopic techniques that include nuclear magnetic resonance (NMR), Fourier transform infrared spectroscopy (FTIR), and ultraviolet (UV) absorption. Computer simulation and combinatorial screening of resulting polymer performance can also be used. The sorbent–analyte interactions in solid format can also be analyzed by solid-state NMR, calorimetric, and FTIR. All the above methods have been reviewed [67]. The NMR spectra of individual monomer and template are compared to that of the monomer–template mixture. The NMR chemical shifts give an idea of the strength of the template–monomer interactions. For FTIR, template–monomer interactions, especially those due to hydrogen bonding, can easily be identified. The FTIR stretching frequency of amino groups (hydrogen bond donors) and carbonyl groups (hydrogen bond acceptors) are displaced, and an observable shift occurs [67]. However, the presence of some interferant solvents may hinder the process, hence, explaining why FTIR is not much applied in monomer–template solutions but in the formed solid sorbent. General examples of where FTIR was used to evaluate template–monomer interaction were discussed by Karim et al. [67].

The UV method is based on comparison of the UV spectra of individual compounds of ligand and Cr(VI) to that of a mixture in solution. Presence or absence of absorption bands is an indication of ligand–Cr(VI) interaction. The method is very simple, and its use in template–monomer interactions in general has been reviewed [67]. Cr(VI) does absorb UV light, and therefore it is easy to study its interaction with possible ligand in solution. Computer simulation and a combinatory approach have so far been reported for organic compounds in magnetic ion-imprinted polymers (MIIPs) and not IIPs, in particular for Cr(VI). Computer simulation is of interest because if one has to experimentally vary different monomers and with various amounts, it demands a large number of experiments. One potential solution to the problem lies in molecular modeling and in performing thermodynamic calculations. Piletsky et al. [68] has been at the forefront for development of models. However, for the computer model to work well, it has to take into account various factors including the structure monomers and templates,

and possible interactions with templates, solvent, and other molecules. An extremely large computational workload is required for such complex systems, and that is a challenge.

Techniques for characterization of the sorbents

Many techniques can be used to evaluate the prepared sorbent. The information one can gather will differ with each technique. Therefore, to get as much information as possible a number of them are used. Important information extrapolated includes Cr(VI)–sorbent interaction, size, shape and morphology, composition of the sorbent, surface area of the sorbent material, hydrophobicity of the sorbent, etc. All the factors are important in sorbent performance. Solid-state NMR can be used to characterize both the sorbent and the Cr(VI)–sorbent interaction within the prepared polymer. However, its use is limited due to the highly amorphous and heterogeneous nature of the polymer which leads to unexplainable NMR spectra of broad or overlapping chemical shifts. NMR demands that the polymer structure be a little crystallizable and has rarely been reported for Cr(VI) sorbents.

The use of FTIR to investigate solid sorbents is simpler and can be used directly without other constituents, which interfere with the determination of polymer functionalities. The FTIR method is very common and almost a must in sorbent characterization [7,21,40,69]. It can be used to evaluate the composition of the polymer as well as if certain functional groups are present or not [7,21,40,69]. It can also be used to study the Cr(VI)–sorbent interaction by looking at the position of spectra due to certain function groups and their shift in the presence of the Cr(VI) [19].

Another important technique is the energy-dispersive spectrometry (EDS) which provides useful information about the elemental distribution on the sorbent especially for IIPs and MIIPs by elemental mapping of each component. For example, after ion imprinting, if the IIP is compared with non-IIP, the presence or absence of the Cr(VI) can be confirmed. EDS can also be used to check whether the entire metal ion (template) has been leached during washing of IIPs. Total leaching of metal ion from IIPs prevents bleeding of the template during polymer usage. It can be combined with other analytical techniques like AAS that measure the leached metal ion in solution. Mass balance calculations can then be made. EDS can be complimented by powder X-ray diffraction (PXRD). PXRD allows characterization of elemental composition of the sorbent [22]. Magnetite in PXRD pattern display six characteristic peaks for Fe_3O_4 (2θ = 30.1°, 35.5°, 43.1°, 53.4°, 57.0°) marked by their indices (220), (311), (400), (422), (511), and (440) [70]. To account for the stability of magnetite sorbents, the amount of iron present can also be measured using AAS after leaching with suitable acid.

Surface area, pore volume, and average pore diameter of sorbents including IIPs are determined with Brunauer–Emmett–Teller (BET) calculations [19,40]. The capacity and kinetics of Cr(VI) binding on the sorbent is generally linked to parameters measured from BET besides the actual chemistry of the sorbent surface. BET measurements are therefore very important in sorbent characterization. A polymer with many micropores on the spherical surface facilitates the fast binding of the template ions [71].

Scanning electron microscopy (SEM) is used to look at the shape, size, and morphology of the polymers [7,40]. A smooth surface is good for homogeneous binding of Cr(VI). Another technique similar to SEM but with higher resolution is transmission electron microscopy (TEM) [21]. TEM is based on detecting differences in electron density identified as contrast changes in the image [70]. TEM is commonly used to study nanoscale heterostructures. In magnetic polymers, magnetite is used as a nano starting material and TEM images provide useful information as to whether the Fe_3O_4 particles are still intact in the polymer matrix or have been leached out. TEM can allow following the increase in diameter of the sorbent as it is being modified besides the morphology [21]. TEM micrographs have provided sizes of composite particles and revealed their monodisphere nature [21,70].

Thermal stability of sorbents is studied by thermal gravimetric analysis (TGA) [19,21,60]. The sorbent is heated from say 25 to 400 °C with a heating rate. The change in polymer mass is followed. Most polymers are stable up to 130 °C. The composition of the polymer can be followed to some extent since polymer components start being lost as temperature increases [21]. For magnetic sorbents and

IIPs, final TGA analysis does not reach zero because of the metal ions present in such materials. The presence of magnetite in the material can further be confirmed using vibrating sample magnetometer (VSM). VSM permits constructing a magnetization curve to determine the relationship between magnetization (M) and magnetic field (H) [21,70]. Using controlling and monitoring software, the system can tell you to what extent the sorbent are magnetized and how its magnetization depends on the strength of the constant magnetic field.

DETERMINATION OF Cr

Determination of Cr can be achieved by several methods. The methods used may differ in terms of accuracy. In adsorption methods, Cr(VI) can be determined from the aqueous samples after passing the adsorbent or following adsorption the sorbents are leached with a suitable solution (e.g., NaOH). Then, Cr(VI) is determined from the leachate using the 1,5-diphenylcarbazide spectrophotometric method. 1,5-Diphenylcarbazide is a chromogenic reagent that forms complexes with chromate anions absorbing at 540 nm. Due to its selectivity for Cr(VI), numerous researchers have used it for the determination of Cr(VI) [5–7,9,10,17,21,29,56]. The method is simple, easy, eliminates Cr(III) uncertainties due to reduction, and is less expensive as it only involves a UV/vis spectrophotometer. Therefore, one might expect that each laboratory will have at least one UV/vis instrument. Flame AAS [8,10,17,18,36], ICP-OES [33], or inductively coupled plasma mass spectrometry (ICP-MS) [72] may be used for total Cr determination. The validity of these methods is enhanced if samples are subjected to oxidative conditions in order to covert all Cr(III) into Cr(VI). However, some researchers have reported Cr(VI) concentrations with AAS, ICP-OES, and ICP-MS [8,18,29,38,72,73,74]. The reliability of these results cannot be totally trusted due to possible reduction of Cr(VI) to Cr(III) under acidic conditions. That is, adsorption capacity values quoted could be inflated due to the presence of Cr(III) since calculations are based on total Cr. Cr(VI) determinations were achieved using high-performance liquid chromatography (HPLC) with post-column derivatization and UV/vis detector at 540 nm [19,75]. Eluent comprised of a mixture of ammonium hydroxide (100 mM) and ammonium sulfate (250 mM). Post-column derivatization reagent was a mixture of 1,5-diphenylcarbazide reagent (2 mM), 10 % methanol, and 0.5 M H_2SO_4. Post-derivatization method is quite easy and a more effective method for determination of Cr(VI) concentration as it eliminates interferences. This is perhaps one of the best determination methods for the speciation of Cr(VI).

GENERAL COMPARISON OF SORBENT PERFORMANCE PARAMETERS

Table 1 shows that research on finding highly efficient polymeric adsorbents for the removal of Cr(VI) is on track. Taking an average of adsorption capacity values over different years suggests an improvement. It is particularly pronounced when one compares earlier literature to that of 2011–2012. The higher capacity of the sorbent is very important in applications to real samples, the reason being that possible competition for adsorption with SO_4^{2-} anions is known [8,18,19,24,40,76]. The high capacity of the polymer allows the Cr(VI) to be extracted even in the presence of competitors. The situation could be different for selectivity polymers such as IPPs. In selective polymers, the cavities might still be large enough to allow co-extraction of other competitors like F^- [19].

The synthetic polymeric sorbents or modified natural sorbents in theory should have high selectivity and fast mass-transfer kinetics because the final functional groups of the sorbents are tailored to bind Cr(VI). However, in several publications selectivity studies were often not conducted, making it difficult to compare performance based on this aspect. The equilibration time seems to depend on the actual sorbent and not the type. However, on average, synthetic polymeric sorbents and modified natural sorbents seem to have low equilibration time, thus fast mass-transfer kinetics. Equilibration time of ca. 20–60 min is most common for synthetic polymers, while for biosorbents that time is around or greater than 120 min (Table 1). Most sorbents regardless of the type work best in acidic pH of the sam-

ple, a pH range of 2–2.5 being the most common followed by pH 3 and then pH 4. Thus, sample pH of 2–4 is generally the most ideal in many sorbents reported so far (Table 1), perhaps expected since Cr(VI) is negatively charged so a sorbent with positively charged functional groups is needed (i.e., protonation pH for organic compounds). Most amine-based functional groups work best in acidic media that favor the protonation of the functional group [21]. In a few cases, sorbents with optimum sample pH > 5 have been reported [23,36,86,89]. It shows that such sorbents are less affected by the concentration of hydroxide ions at higher pH. The Cr species adsorbed at pH > 6 is the CrO_4^{2-} that is usually at lower concentration relative to other Cr(VI) species [40,56,60]. Duranoglu et al. [40] observed the reduction of Cr(VI) to Cr(III) during the adsorption of the former onto activated carbon derived from acrylonitrile-divinyl benzene copolymer at sample pH of 2 and not at pHs 4, 6, and 8. The overall adsorption might not be influenced if the produced Cr(III) is also adsorbed on the sorbent, especially if total Cr is measured. However, if only the diphenylcarbazide method is employed to measure Cr(VI) then there will be low recovery of Cr(VI). The reduction process could lower the amount adsorbed if sorbents selective for Cr(VI) are used. Though sample pH 2–2.5 is the most optimum in Table 1, caution must therefore be taken depending on the sorbent and reactions occurring in the system.

The application of prepared sorbents is to remediate polluted wastewaters such as acid mine drainage water. pH of such wastewaters is generally acidic [19]. Most reported polymers therefore could be suitable for application to polluted wastewaters as the showed maximum adsorption at low pH. It is with regret that many researchers did not do any applications to real samples to prove the adsorbents. A disadvantage of working at low pH is that samples may have very high concentration of SO_4^{2-}, which is one of the major competitors for Cr(VI) adsorption. Duranoglu et al. [40] studied the effect of various anionic competitors (Cl^-, NO^{3-}, SO_4^{2-}, PO_4^{3-}) during Cr(VI) adsorption onto activated carbon derived from acrylonitrile-divinyl benzene copolymer at sample pH 2. Factors that influence adsorption of competitors include size, charge, and hydration degree. A maximum drop in adsorption of Cr(VI) by the sorbent was experienced with PO_4^{3-} [40], the reason being that PO_4^{3-} has more negative charges and is also polyatomic with similar molecular dimensions and consequently the same hydration degree as Cr(VI) [40]. Cl(V) has a similar charge with Cr(VI) but has higher charge density due to the small molecular dimensions. However, it has higher hydration than $HCrO_4$. Cl^- therefore had the least influence on adsorption of Cr(VI). In the pH range of 1–6, Cr ions coexist in forms of $Cr_2O_7^{2-}$, $HCrO_4^-$, $Cr_3O_{10}^{2-}$, and $Cr_4O_{13}^{2-}$ of which $HCrO_4^-$ is the most dominant while at higher pHs, CrO_4^{2-} and $Cr_2O_7^{2-}$ are the most dominant species [69].

New sorbent development for Cr(VI) also involves studies on how it is adsorbed on the sorbent and the kinetics of adsorption. Although not part of the review, generally, Langmuir and Freundlich models are used to study the adsorption of the analyte onto a sorbent. The Langmuir model is valid for monolayer adsorption on a surface containing a finite number of identical sites [22,69]. The Freundlich model assumes adsorption on heterogeneous surface with non-uniform distribution of energy of adsorption [77]. Kinetics of Cr(VI) adsorption involve using pseudo-first- and second-order models [22,77].

CONCLUSIONS

From the results in Table 1, it is evident that a range of adsorbents have been prepared and used for Cr(VI) adsorption. Adsorption capacity results and equilibration time achieved are rather scattered but further scrutiny does suggest which types of sorbents should be explored in future. It is known that different laboratories have different budgets, therefore the literature that is coming through is to some extent influenced by budget. Therefore, less appropriate reagents and conditions might be used. Electrostatic interaction seems to be the popular mechanism for Cr(VI) removal. However, electrostatic interaction is due to physical adsorption and is nonspecific [62]. Therefore, there is still a need to produce more specific and selective polymeric sorbents for Cr(VI). Moreover, as alluded to in the text, several researchers have not examined the selectivity of their sorbents, taking into account the nonspecificity of electrostatic interactions, therefore one may conclude that specific and selective polymers for

Cr(VI) is the future. It seems the use of acrylate for Cr(VI) does not give good adsorption results. On the other hand, PPy polymers gave higher adsorption capacities particularly when they were combined with bamboo-like nanotubes [48]. PPy backbone is similar to 1,5-diphenylcarbazide structure, which is a specific reagent for Cr(VI) determination. Modification of PPy could produce sorbents with better specificity and selectivity for Cr(VI). The lack of development of selective materials could be attributed to the challenges of preparing imprinted polymers using chromate as a template.

FUTURE DIRECTION

A future trend is likely to move onto pilot studies accompanied with cost evaluation of the developed systems. This is important because the focus so far has been laboratory studies of different sorbents for Cr(VI) adsorption from the analytical and materials science point of view.

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