Chromium removal from water using modified organic materials: A review

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ABSTRACT

Chromium is a non-biodegradable element predominantly found in two chemical forms, Cr(VI) and Cr(III). Several remediation strategies have been implemented to achieve its removal from aquatic environments with limited results. This review article focuses on the analysis of removal strategies including the use of: (1) raw materials (agro-wastes, activated carbons, extracts and solutions) and (2) treated materials (alkaline and acid treatments). The article also reviews and analyses results obtained with surfactant modified organic biomasses. Although this review aims to summarise chromium removal techniques by highlighting relevant results of several studies, surface modification is outlined as a promising method to improve removal efficiency in aqueous solutions. The information presented in this article can help in the development of more efficient methods considering the improvements that surfactants may offer.

Key words | adsorption, chromium, heavy metals, remediation, water

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INTRODUCTION

Across the world, millions of people live in areas where water is physically scarce. Spills, seepages, leachates from mining processes, land disposal of solid wastes, and effluents from industries have resulted in the accumulation of heavy metals in water. Heavy metals are harmful elements, non-biodegradable and bioaccumulable in plant and animal tissues. They represent a great concern owing to their persistency in the environment, but in trace concentration are essential for living organisms (Bollinger *et al.* 1997; Davidson *et al.* 1998; Jain & Ali 2000; Maine *et al.* 2004; Dwivedi *et al.* 2010; Wu *et al.* 2016). It has been widely accepted that the bioavailability and the mobility of heavy metals is determined by the chemical speciation, which in turn is controlled by pH, temperature, salinity and organic matter (OM) content. pH is a critical parameter related to the adsorption of heavy metals because a small change can alter the speciation and bioavailability in solution. In fresh waters, a change of 0.5 pH unit can either represent the adsorption or desorption; in soil, the degree of sorption increases rapidly over a narrow pH range that determines the cation or anion adsorption onto oxide minerals. Salts and metals can occur in both soil and water. Acosta *et al.* (2011) indicate that salinity increases the mobilisation of heavy metals in soils, but the process is complex and will depend mainly on the type of heavy metal, its total content and the type of salt involved (Du Laing *et al.* 2008). Zhao *et al.* (2013) found that salinity can cause elevated mobility of cadmium (Cd), copper (Cu), manganese (Mn) and lead (Pb) in estuarine sediments, but can also elevate the potential ecological risk of Cd and Mn. Sodium (Na) and magnesium (Mg) promote Cd release from sediments (Greger *et al.* 1995), whereas chloride ions can form complexes with zinc (Zn), Cd and Cu in sea water (Fritioff *et al.* 2005). Heavy metal ions react in the presence of OM in soils, sediments and aquatic systems through adsorption, complexation and chelation mechanisms. OM typically

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consists of diverse oxygen-containing functional groups, such as carboxyls, phenols, enols and alcohols that can create complexes with polyvalent heavy metal cations. Additionally, amines, azo groups, heterocyclic nitrogen compounds, ethers and carbonyls are able to form coordination linkages with metal ions (Kaschl & Chen 2005).

CHROMIUM POLLUTION

Chromium (Cr) may exist in natural water bodies in concentrations below 50 μg/L (Richard & Bourg 1991; Kotaś & Stasicka 2000). This metal mainly occurs either in the trivalent state, Cr(III), or in the hexavalent state, Cr(VI), with different toxicity and environmental behaviours (Figure 1).

The trivalent form is poorly soluble and is considered an essential nutrient for plant and animal metabolism, but prolonged exposure may cause health problems in humans (Anderson 1997; Zhang *et al.* 2008). Cr(III) oxidises in the presence of manganese oxides, and forms stable complexes with organic ligands that eventually settle (Bartlett & James 1979; Nakayama *et al.* 1981; Young & Harvey 1992; Fendorf 1995). In soil, the adsorption of Cr(III) increases with the content of organic matter as more sites are present for sorption to occur, and with increasing pH, due to deprotonation of adsorbent surface. In solution Cr(III) adsorption decreases in the presence of competing cations or dissolved organic ligands (Bradl 2004). Cr(VI) is highly mobile and soluble. It is a powerful carcinogenic and teratogenic toxic pollutant (Léonard & Lauwerys 1980; Richard & Bourg 1991; Cieślak-Golonka 1996; Rodríguez *et al.* 2009) that can induce skin and liver damage, and is detrimental to the respiratory system (Baranowska-Dutkiewicz 1981; Kornhauser *et al.* 2002; Nityanandi & Subbhuraam 2009; Khlifi *et al.* 2013; Das *et al.* 2015). In water, Cr(VI) is reduced in the presence of electron donors and OM (Rai *et al.* 1989; Richard & Bourg 1991; Fendorf 1995; Mattuck & Nikolaidis 1996); in soil, regardless of the soil pH, OM can reduce Cr(VI), with limited influence when the OM is fresh or little degraded (Fendorf 1995). At low pH, other soil molecules containing hydroxyl groups are able to adsorb Cr(VI). Several studies have suggested that the Cr(VI) adsorption mechanism involves primarily ion-exchange, electrostatic attraction, Cr(VI) reduction to Cr(III), and complexation. Islam *et al.* (2019) indicate that Cr(VI) sorbs onto mineral surfaces by inner-sphere complexes at pH below 6.0, while outer sphere complexes tend to dominate at higher pH values, but, in general, sorption of Cr(VI) decreases with increasing pH while at low pH values, surfaces will be neutral or positively charged, leading to higher adsorption due to opposite charge attraction.

Treatments for minimising the content of chromium in water include osmosis (Qdais & Moussa 2004; Cui *et al.*

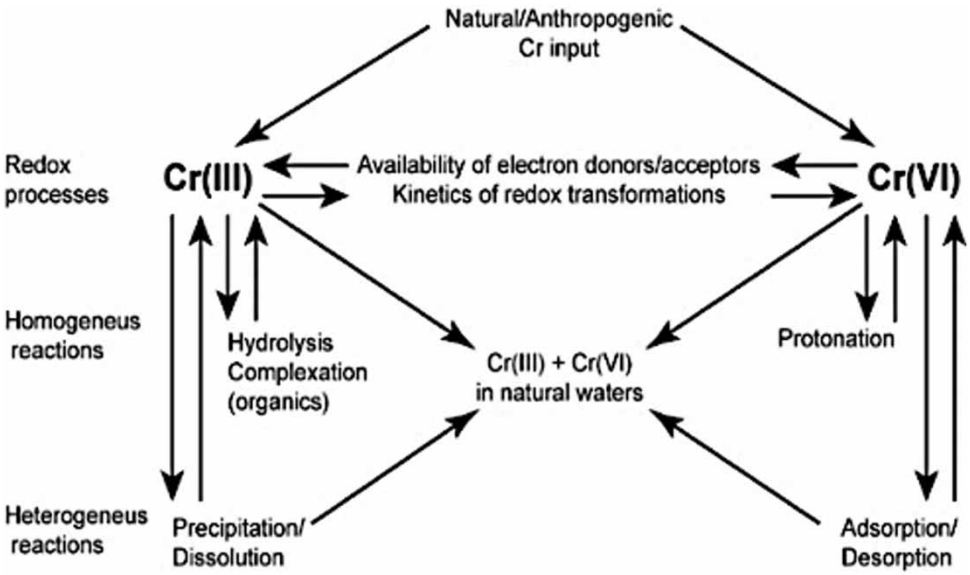

Figure 1 | Aqueous geochemistry of chromium, taken from Richard & Bourg (1991).

2014), ion-exchange (Dąbrowski *et al.* 2004), coagulation and precipitation (Charerntanyarak 1999), the application of advanced materials (nanoadsorbents, nano-enhanced membranes, nanometal oxides, nanophotocatalysts) (Hafiane *et al.* 2000; Suthar & Gao 2017) and biopolymers made of cellulose, lignin, proteins, etc. (Gutnick & Bach 2000; Pérez *et al.* 2006; Singha & Guleria 2014). Adsorption is an effective process, especially to remove low concentrations of metal ions. Conventional adsorbents include inorganic materials such as activated carbons (ACs), zeolites and clays. Although ACs are a powerful adsorbent, in recent years the research into new, environmentally friendly and low-cost adsorbents has increased; in this context, agro-wastes are frequently applied.

RAW MATERIALS FOR CHROMIUM REMOVAL

Diverse organic materials require little or no processing before their application in water treatments, hence, throughout this paper the term 'raw' will refer to those used without processing with acids, bases or other chemicals. Raw materials such as fungal, algal and bacterial biomasses exhibit considerable biosorption properties related to the presence of carboxyl, imidazole, sulfydryl, phosphate, sulfate, sulfonate, thioether, phenol, carbonyl, amide and amino moieties (Gardea-Torresdey *et al.* 1990; Tobin & Roux 1998; Sudha Bai & Abraham 2001; Park *et al.* 2005; Bishnoi *et al.* 2007; Ertugay & Bayhan 2008; Gupta & Rastogi 2008; Li *et al.* 2008; Wang & Chen 2009) and are applied either fresh or dried (Park *et al.* 2005; Liu *et al.* 2007). For instance, fungi such as *Mucor racemosus* (Tobin & Roux 1998; Liu *et al.* 2007) and *Candida* sp. LMB2 (Juvera-Espinosa *et al.* 2006) have been used for the removal and reduction of Cr(VI), whereas the mycelia of *Rhizopus* and *Aspergillus* has been reported to adsorb the same metal species (Coreño-Alonso *et al.* 2014). Micro-algal biomass can be applied either fresh (with moisture) or dried after the separation of the solid fraction (Gupta & Rastogi 2008). For application, macroalgae such as *Nostoc muscorum* generally requires only to be dried and ground (Bishnoi *et al.* 2007; El-Sikaily *et al.* 2007). *N. muscorum* was reported to remove up to 22.92 mg/g of Cr(VI) at pH 3.0 (Gupta & Rastogi 2008). Functional groups reported to be associated with the adsorption of Cr(VI) and sequestration of Cr(III) are the amino, using *Chlorella miniata*, and carboxylates or carbonyls using *Chlamydomonas reinhardtii* (Arıca *et al.* 2005; Han *et al.* 2006, 2007). *Spirogyra* spp. and *Oedogonium hatei* are other examples of marine and freshwater algae used for the biosorption of Cr(III) and Cr(VI) from aqueous solutions (Bishnoi *et al.* 2007; Gupta & Rastogi 2009).

Agro-wastes

Agro-wastes are typically composed of lignin and cellulose. Lignin accounts for up to 33% of the plant biomass and gives vascular plants the structural strength needed to stand upright and to protect the cellulose and hemicelluloses. Some agro-wastes only require water washing, drying and grinding before direct application into a chromium solution. For example, orange waste and ectodermis of *Opuntia* were applied for the sorption of up to 77% Cr(III) and 99% Cr(VI). This affinity was attributed to the presence of hydroxyl, methyl and carboxyl moieties (Barrera *et al.* 2006; Pérez-Marín *et al.* 2009). In solution (pH 4.0), tamarind seed, almond shell, ground nut shell, walnut shell and coconut shell have been reported to remove up to 80%, 36%, 35%, 40% and 30% of Cr(VI), respectively (Agarwal *et al.* 2006). Suhas *et al.* (2007) suggested that lignin is the main component responsible for metal adsorption due to the presence of alcohols, aldehydes, ketones, carboxylic, phenolic and ether groups (Demirbas 2008). Wassie & Srivastava (2016) indicated that the Cr(VI) reduction can occur either by the binding of Cr(VI) species to amino and carboxyl groups, followed by the reduction of Cr(VI), or by the contact of the metal with the electron-donors on the surface of teff straw. Moussavi & Barikbin (2010) also suggested that the amino, carboxyl and hydroxyl moieties are involved in the adsorption of Cr(VI) using green pistachio hull. An extensive review on lignocellulosic materials, including wood and agricultural residues, can be found in Miretzky & Cirelli (2010).

Activated carbons (ACs)

ACs are adsorbents broadly applied in wastewater treatments, owing to their high surface area and high

adsorption capacity (Toles *et al.* 1999; Mohan & Pittman 2006). ACs prepared from algal biomass, fruit shells, agro-wastes, sawdust, etc., may represent an accessible alternative to existing commercial products, and diverse authors have reported a considerable efficiency using them (Table 1). Functional groups reported in ACs prepared from nutshells include carbonyls, phenols, lactones and carboxyls (Toles *et al.* 1999).

Extracts and solutions

Extracts and aqueous solutions have also been successfully applied. Najim *et al.* (2014) reported the removal of up to 95% of Cr(VI) at pH 2.0, using peppermint leaf extracts, highlighting the presence of amino and hydroxyl moieties. Mystrioti *et al.* (2016) used polyphenols from aqueous solutions of green tea, clove, spearmint extracts, pomegranate juice and red wine to prepared nano-iron suspensions to reduce Cr(VI) in water.

CHEMICAL TREATMENTS FOR CHROMIUM REMOVAL

Since raw materials can cause high chemical oxygen demand (COD), biological chemical demand (BOD) or a high total organic carbon (TOC) content, they are often modified to improve their properties (Wan Ngah & Hanafiah 2008). These treatments may include the use of alkaline solutions (sodium hydroxide, calcium hydroxide, sodium carbonate), acid solutions (hydrochloric acid, nitric acid, sulfuric acid, tartaric acid, citric acid, thioglycollic acid), organic compounds (ethylenediamine, formaldehyde, epichlorohydrin, methanol), oxidising agents (hydrogen peroxide), etc. (Wan Ngah & Hanafiah 2008). Specifically, the alkaline and acid treatments expose metal binding sites or remove/mask certain functional groups. However, the nature of the raw material will determine the results of a chemical treatment; for example, the metal uptake capacity of a fungal biomass increases using an acid treatment, contrary to the application of an alkaline treatment, which may have little influence on the metal adsorption capacity of the biomass (Wan Ngah & Hanafiah 2008; Wang & Chen 2009).

Boiling and/or formaldehyde treatments have been used to eliminate colour and water-soluble substances from rice husk (Bansal *et al.* 2009), coffee husk (Oliveira *et al.* 2008), eucalyptus (*Eucalyptus globulus*), bark (Sarin & Pant 2006) and ectodermis of *Opuntia* (López-González *et al.* 2012). The treatment consists of boiling the raw material in distilled water for several hours, then washing and drying. The product is subsequently sieved, treated with formaldehyde and dried, ready to use or for further modifications. Jain *et al.* (2009) compared boiling vs formaldehyde treatments for the removal of Cr(VI) using sunflower stem waste and indicated that the boiled stem had a slightly better performance than the formaldehyde stem (32.4% and 31.3%, respectively, at pH 2.0). López-González *et al.* (2012) also compared the performance of formaldehyde and HCl on the ectodermis of *Opuntia* for the removal of Cr(VI) and found that the maximum Cr(VI) sorption rate (~73%) occurred at pH 2.0 using both treatments, but equilibrium was first reached using HCl. On the other hand, the application of salts ($CaCl_2$) on algal biomass promotes the removal of Cr(III) (Bishnoi *et al.* 2007), whereas the use of Na-alginate in combination with $CaCl_2$ for the manufacturing of Ca-alginate beads has been applied to remove up to

Table 1 | Reported efficiency of Acs

Type	Efficiency (%)	pH	Reference
U. lactuca	98	1.0	El-Sikaily *et al.* (2007)
Olive waste	97	2.0	Demiral *et al.* (2008)
Aegle Marmelos (fruit shell)	82.3	2.0	Gottipati & Mishra (2016)
Peanut shell	40	2.0–4.0	Al-Othman *et al.* (2012)
Longan seed	62	3.0	Yang *et al.* (2015)
Rice husk	81–94	2.0	Guo *et al.* (2003); Bishnoi *et al.* (2004); Sugashini & Begum (2015)

80.6% and 41.5% of Cr(VI) and Cr(III), respectively (Ullah *et al.* 2013).

Alkaline treatments

Alkaline treatments can be a previous step for acidic modifications. For example, after the application of NaOH on wheat bran the biomass may be protonated with HNO_3. The preparation of alkaline wheat bran starts with the addition of the husk into a NaOH solution, then the mixture is autoclaved to remove the low molecular weight lignin compounds, filtered, washed and dried (Krishnani *et al.* 2008). The functional groups associated with the chromium removal are typically alcohols and carboxyls, generated from the oxidation of lignin compounds (Dupont & Guillon 2003). Besides the removal of Cr(VI), NaOH-treated rice husk can support the reduction of Cr(VI) to Cr(III) under acidic conditions, wherein lignin and carboxylic functional moieties act as electron donors (Krishnani *et al.* 2008). In the work of Bishnoi *et al.* (2007), the application of NaOH on *Spirogyra* sp. increased the Cr(III) adsorption capacity of the biomass, from 10.51 mg/g using the raw alga to 11.45 mg/g using the alkaline material. The treatment consisted of suspending the alga in a NaOH solution for several hours, with subsequent washing and drying. Other wastes such as banana peel can go through alkaline hydrolysis to break up the cellulose chains and to form smaller monomers. This product needs to be further treated with $NaClO_3$ and glacial acetic acid (Ali *et al.* 2016).

Acidic treatments

When acidic treatments are applied on algal cell surfaces, diverse functional groups, such as amino, carboxylic, hydroxyl and carbonyl can be exposed, especially amino groups and carboxyls (Gupta & Rastogi 2009). As an example, the acidic treatment of *C. reinhardtii* consisted of the addition of the raw biomass into an HCl solution, the separation of the solid/liquid fractions, washing with a saline solution, drying and grinding (Arıca *et al.* 2005). H_2SO_4 has been applied to *Sargassum* (Kratochvil *et al.* 1998) and *Ecklonia* (Park *et al.* 2004) to replace ionic species with protons and sulfates. *Ecklonia* biomass removed Cr(III) through an ion-exchange mechanism and Cr(VI) through a redox reaction with the biomass. In the case of *Sargassum*, the acidic biomass required an extra wash with $Ca(OH)_2$; this material was found to be an effective biosorbent for Cr(VI) at pH 2.0 and also capable of removing substantial quantities of Cr(III) at pH > 3.0.

Acid-treated *Eucalyptus* bark was reported to remove approximately 99% of Cr(VI) at pH 2.0. The acidic bark was produced by adding clean bark into a solution of formaldehyde/H_2SO_4. The mixture was stirred and heated to form a thick slurry, and washed with water until pH > 4.5, filtered and dried (Sarin & Pant 2006). Acidic biomasses of *Agave lechuguilla* and ectodermis of *Opuntia* sp. have also been produced using either H_2SO_4 (Barrera *et al.* 2006) or HCl (López-González *et al.* 2012). Barrera *et al.* (2006) indicated that the acidic ectodermis of *Opuntia* removed less substantial amounts of Cr(VI) and Cr(III) compared to the raw material, whereas the acidic *Agave lechuguilla* biomass was successfully used for the binding of Cr(III) (Romero-González *et al.* 2006). Agave bagasse treated with HCl has shown a Cr(III) sorption capacity of 11.44 mg/g at pH 4.0 (García-Reyes *et al.* 2009).

The application of HCl on diverse biomasses typically consists of the addition of the dried biomass into an HCl solution for several hours, followed by water washing or pH neutralisation and drying. Using acidic sorghum straw and acidic oat straw, García-Reyes *et al.* (2009) reported a Cr(III) removal of 6.96 mg/g and 12.97 mg/g, respectively, at pH 4.0. Acidic tamarind seed testa prepared with HCl can remove up to 78% of Cr(VI) (Priya *et al.* 2008). Using banana peel, the HCl de-polymerises the glycoside linkage in hemicelluloses and lignin through α- and β-aryl ether cleavage to soluble products (Ali *et al.* 2016). Carboxylic groups from banana peel can be esterified using a treatment with acidic methanol. Amines, carboxylic groups, acid groups and hydroxyl groups were suggested to be involved in the removal of Cr(VI) (Memon *et al.* 2008). Citric acid has also been applied to increase the metal ion adsorption capacity of soybean hull (Marshall *et al.* 1999). The method uses a NaOH solution mixed with the hull and citric acid. To remove the citric acid excess, the material required water washing and suspension in water for the addition of $Pb(NO_3)_2$. It was suggested that the citric acid forms citric acid anhydride, which is combined with the cellulosic hydroxyl group to form an ester linkage, and

introduces a carboxyl group to the product that increases the binding with positively charged metal ions. A similar procedure, but using other carboxylic acids, has also been applied on rice husk for the removal of copper and lead (Wong *et al.* 2003). The acidic treatment of sugar cane bagasse using succinic acid consists of the removal of the soluble sugars by boiling the biomass, oven drying and grinding. The acid-treated sugar cane is then polymerised with acid, washed with double distilled water, oven-dried and sieved (Garg *et al.* 2009). The maximum removal of Cr(VI) reported for the modified sugar cane was of 92% at pH 2.0.

Surface modifications

Surfactants are long-chain molecules composed of both hydrophilic and hydrophobic parts (Figure 2) extensively used for the modification of inorganic substrates. In an aqueous solution, at the critical micellar concentration (CMC), surfactants form micelles that behave as large molecules (Nivas *et al.* 1996). At concentrations above the CMC, surfactants can form other structures, such as spherical micelles, cylindrical micelles, worm-like micelles, lamellar formation or vesicles. These structures are continuously forming and disintegrating (Rosen 2004).

Tetra methyl ammonium (TMA), hexadecyl trimethyl ammonium (CTA), n-cetylpyridinium benzyltetradecyl ammonium (BTDA), stearyl dimethyl benzyl ammonium (SDMBA), etc. are among the molecules employed for the modification of inorganic surfaces. Figure 3 shows a general model of the modification of a solid surface via the sorption of an ionic surfactant.

Modification of organic biomasses

Saccharomyces cerevisiae modified with cetyl trimethyl ammonium bromide (CTAB) has been used to remove Cr(VI) (Bingol *et al.* 2004). The modification consists of washing the biomass with water and the separation of the

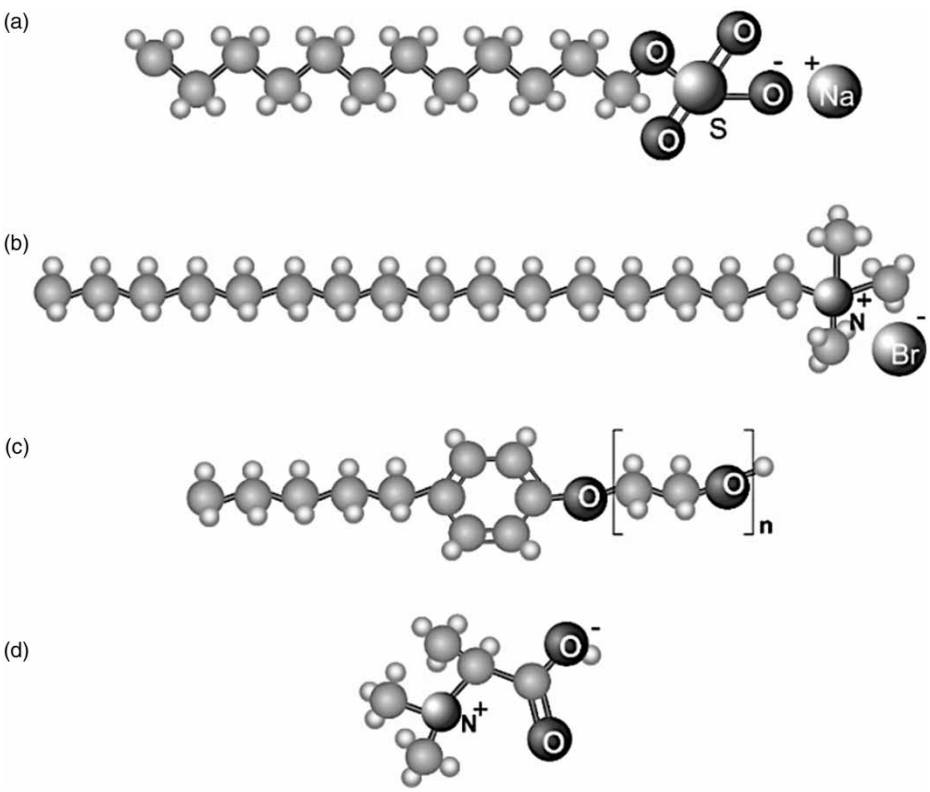

Figure 2 | Molecular structure of (a) anionic surfactant, sodium dodecyl sulfate (SDS); (b) cationic surfactant, hexadecyl trimethyl ammonium bromide (HDTMA-Br); (c) non-ionic surfactant, Triton X-100 (TX-100); (d) zwitterionic surfactant, trimethyl glycine (TMG).

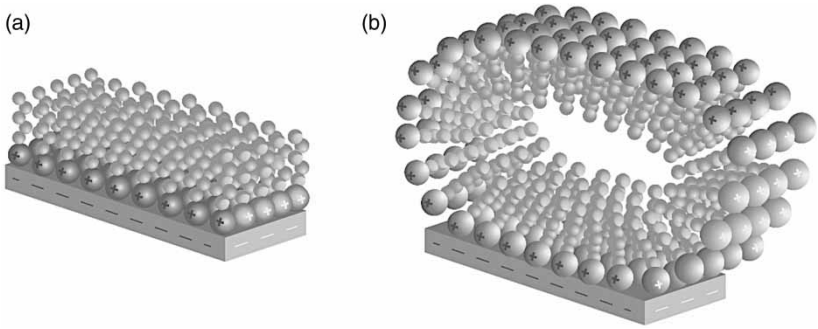

Figure 3 | General model of the modification of a solid surface: (a) forming a positive monolayer (hemimicelle) and (b) forming a positive bilayer (admicelle).

solid and liquid fractions followed by oven-drying. The resulting material is mixed with a surfactant solution. It was suggested that the non-polar portion of the surfactant interacted with the cell surface making the surface potential positive, resulting in a Cr(VI) removal of 80%, higher than that observed using unmodified yeast (55%). Clean and dried particles of the mushroom *Tricholoma lobayense* have been modified using the cationic surfactant dodecyl dimethyl benzyl ammonium bromide (DDBA-Br). The modification consists of the addition of the powdered biomass into a surfactant solution with agitation for several hours. The mixture was subsequently filtered and washed until no bromide was left in the filtrate and dried. The maximum adsorption capacity reported was up to 43.86 mg/g. Functional groups such as carboxyl, hydroxyl, sulfate, phosphate and amino groups were associated with the adsorption of Cr(VI) (Jing *et al.* 2011). Peanut shell modified by amination using cationic surfactants was prepared adding a solution of epichlorohydrin in N,N-dimethylformamide to the biomass, followed by the addition of triethylenetetramine to introduce the amino groups. The mixture was subsequently washed, filtered and dried. Once applied, the modified peanut shell showed a Cr(VI) removal capacity ranging from 92.1% to 95.4% at a pH from 1.0 to 6.0. The functional groups involved were amine and carboxyl groups (Yue *et al.* 2013). Namasivayam & Sureshkumar (2008) modified coir pith using hexadecyl trimethyl ammonium bromide (HDTMA-Br). Briefly, the procedure consisted of mixing the dried and homogenous particles of coir pith with HDTMA-Br for several hours. Afterwards, the liquid phase was discarded and the solid phase was washed with distilled water several times to remove the superficially held surfactant. It was suggested that the mechanism driving the sorption of the surfactant on the biosorbent was the interaction of the non-polar (alkyl) portion of the surfactant with the coir pith surface through hydrophobic bonding and the polar (positively) charged head groups pointed towards the bulk of the solution, making the surface potential positive. Electrostatic attraction of surfactant cations on the negatively charged coir pith surface is another possible mechanism. As a result of both potential mechanisms, the modified biosorbent offers a positive surface into which the anionic Cr(VI) is attracted. In the work of Kalidhasan *et al.* (2012), a dried powder of a cellulose biopolymer was modified with tetrabutyl ammonium iodide (TBAI). The clean and dried cellulose biopolymer was mixed homogeneously with TBAI, microwaved, washed with water until reaching neutral pH and dried. It was suggested that the interaction of the ionic head group of the surfactant with the cellulose through electrostatic and hydrophobic effects played an important role in the adsorption of Cr(VI). Hexadecyl pyridinium bromide (HDP-Br) applied to rice husk has produced a modified material with higher Cr(VI) removal efficiency compared to the initial raw husk (Ali *et al.* 2015). Surfactant modified coir pith has been prepared with HDTMA and has shown a Cr(VI) adsorption capacity of 76.3 mg/g at an optimal pH of 2.0 (Namasivayam & Sureshkumar 2008). Other available examples require the addition of the surfactant into aqueous solutions and water extracts of mango leaves, *Azadiracta indica* and sajina flower. The extract of mango leaves was prepared by sonicating mango leaf powder in water. This solution was filtered and diluted, followed by the addition of either sodium dodecyl sulfate (SDS) or

TX-100 at a concentration above their CMC. It was suggested that polyphenols, polysaccharides, low molecular weight carbohydrates and proteins present in the mango extract allow the reduction of Cr(VI) up to 75% and 79% using TX-100 and SDS, respectively (Mukherjee *et al.* 2015a). The same authors (Mukherjee *et al.* 2015b) created soluble organo–Cr(III) complexes using surfactant modified extract of *Azadiracta indica*. The mixture of TX-100 or SDS surfactants with water extract of sajina flower was reported to reduce up to 96.25% and 99.37% of Cr(VI) using TX-100 and SDS, respectively (Mukherjee *et al.* 2015c). The functional groups detected in the sajina flower extract were sugars, mainly glucose, and amino acids such as glutamic acid, arginine, proline, tyrosine, isoleucine, leucine, phenylalanine, and aspartic acid. Functional groups responsible for binding of Cr(VI) include carboxyl, amide, polysaccharide and sulfonate.

The application of surfactant-modified activated carbons (ACs) in removal of contaminants from aqueous solutions is possible, but little explored. The Cr(VI) adsorption capacity of ACs modified with cationic surfactants has been reported to be up to five times that of the raw AC (Choi *et al.* 2009). The modification consisted of the addition of the AC into a solution of HDTMA or cetyl pyridinium chloride (CPC), agitation for several hours, filtering and drying (Choi *et al.* 2009). Sodium diethyl dithiocarbamate (SDDC) and TBAI-modified ACs can adsorb ions, copper, zinc, chromium and cyanide (Monser & Adhoum 2002).

CONCLUDING REMARKS

Although heavy metals are essential for life in some forms and in trace concentrations, they represent a major concern for the environment and human health. Specifically, chromium is a hazardous pollutant, the behaviour of which mainly depends on the speciation. In order to reduce the environmental impact induced by chromium discharges in water, the application of bioremediation treatments should be encouraged. Adsorption methods, including raw and treated material have been proved as efficient strategies, mainly using activated carbons, but the associated costs are still high in comparison to other methods. This review suggests that the efficiency of materials such as agro-wastes and diverse biomasses can improve when they are modified; however, the cost/benefit of these modifications is still unknown and requires further evaluation. Still, a huge gap exists between laboratory research and the successful use of adsorption techniques at a large scale. Implementation of these methods at industrial levels requires not only increasing the adsorption capacity and efficiency of the material but also proving the method is a cost-effective alternative.

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