

Physio-chemical treatment technologies for chromium removal

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Abstract. The article reviews the technical applicability of various physio-chemical treatments for the removal of hexavalent chromium (Cr(VI)) from aqueous solution. A particular focus is given to membrane electrolysis, photocatalytic reduction, adsorption and the application of nanotechnology in Cr(VI) removal. About 50 published studies (2011-2017) are reviewed. Liquid membrane and electro dialysis were combined. Metal-organic frameworks (MOFs) emerged to enhance photocatalytic reduction. It is evident that adsorption is the most frequently studied and widely applied for the treatment of Cr(VI). And nanotechnology is mainly applied to nano adsorbent which exhibited both reduction and adsorption capabilities. In general, further researches on methods with cost-effectiveness, technical-applicability, and plant-simplicity are vital for heavy metal removal such as chromium.

Introduction

Chromium (Cr) and its compounds widely used in diverse industrial processes, including alloys and steel manufacturing, metal finishing, electroplating, leather tanning, cooling tower blowdown, or pigments synthesis and dyeing [1]. Most chromium compounds usually start from sodium dichromate or chromate, either directly or indirectly through intermediate steps [2]. In aquatic systems, chromium exists as trivalent (Cr(III)) and hexavalent (Cr(VI)) [3]. Chromium released to the environment poses serious threat to human health [4, 5] due to their carcinogenic and toxicological effects [5]. The toxicity highly depends on its oxidation forms [3]. Cr(III) is about 300 times less toxic than Cr(VI) that is relatively stable and innocuous [6]. Chromium is considered as important priority pollutant worldwide [5]. The US Environment Protection Agency (EPA) recommended maximum drinking water level of chromium (0.1 mg/L) [1]. The World Health Organization (WHO) and the Ministry of Health of China have set the permissible guideline of 0.05 mg/L for Cr(VI) in drinking water [5].

Raising concerns regarding chromium have promoted the researches on chromium removal technologies. Conventional techniques that have been utilized to remove chromium include chemical precipitation, ion exchange, adsorption, membrane, and so on [7]. Chemical precipitation is the most widely used methods. Usually, the precipitation processes make use of hydroxide, sulfide, carbonate and phosphate resulting in Cr-solid state. However, it raised a disposal problem about the sludge [8]. Ion exchange is considered a better alternative, but not appealing because of high operational cost [8]. Compared with others, adsorption is cost effective, easy handling, flexible and selective. To maximize its advantages, researchers show keen interest in low cost adsorbents with

high surface areas and adsorption capacities ^[1, 9]. The increasingly mature nanotechnology promote the application of nanoadsorbent which enhances chemical reactivity and adsorbate/adsorbent interactions ^[1]. On the other hand, various kinds of nanomaterial also enhance the Cr(VI) reduction activity like TiO₂ nanoparticles for photocatalytic reduction ^[10, 11]. This article mainly showed newly technique for Cr(VI) removal including membrane separation ^[6, 12, 13], photocatalytic reduction ^[14, 15, 16], adsorption ^[17, 18, 19], and application of nanotechnology ^[20, 21].

Membrane methods

Membrane methods like ultrafiltration, nanofiltration, reverse osmosis, electrodialysis, and liquid membranes are alternative tools for better separation of Cr from wastewater. Sadyrbaeva proposed a novel hybrid process of galvanostatic electrodialysis and liquid membrane extraction for Cr(VI) removal from aqueous solutions ^[12]. The bulk liquid membrane contained solutions of tri-*n*-octylamine with admixtures of di(2-ethylhexyl) phosphoric acid in 1,2-dichloroethane and was found to be effective for single-stage removal. Besides, it was demonstrated that Cr could be extracted from HCl solutions into dilute solutions of hydrochloric, sulphuric, perchloric, phosphoric acids and water. Optimal conditions of varying ratio of the current, time and concentration are also determined in result of practically complete (>99.5%) removal of Cr(VI) from the feed solution and a maximal stripping degree of ~90% during 1.0-4.0h of electrodialysis ^[12]. Instead, Kaya et. al. employed polymer inclusion membrane under constant electric current for the removal of Cr(VI) from water, which showed excellent selective and long-term use feature and high reproducibility of electric membrane extraction. Besides, polymer inclusion membrane was more stable than the supported liquid membrane. In this study, the Cr(VI) transport was achieved 98.33% after 40 min under optimized conditions ^[13]. Unlike electric membrane extraction, membrane distillation is a thermally driven process and also suitable alternatives to the conventional membrane methods ^[6]. Bhattacharya et. al. set up a modified coupled Knudsen and Poiseuille flow models for the countercurrent direct contact membrane distillation. Hydrophobic polytetrafluoroethylene (PTFE) microporous membrane with polyethylene terephthalate (PET) showed good performance in the experiments. Also, the predictions exhibited good agreement with the experimental results ^[6].

Photocatalytic reduction

As Cr(III) is much less toxic than Cr(VI) and can be easily precipitated and removed as a solid state, reduction of Cr(VI) to Cr(III) are of great important in effective remediation of Cr(VI)-contaminated wastewater ^[10]. Electro-reduction, chemical reduction, and micro-reduction are commonly used, while photocatalytic reduction emerged with more effective and low-cost property, as well as no producing any hazardous chemicals ^[11]. Generally, semiconductor photocatalyst TiO₂ was used due to its durability, low cost, low toxicity, superhydrophilicity, and remarkable chemical and photochemical stability ^[11]. TiO₂ structures are classified into several forms: nanoparticles, microspheres, nanrods, and nanosheets ^[14, 15, 16]. And the TiO₂ hollow sphere structure has raised considerable attention because of its low density, large surface area, good surface permeability, and great light-harvesting capacity. As the cavity sizes in the hollow sphere determine the photocatalytic reactivity and efficiency to a great extent, Cai et. al. studied the controllable size of TiO₂ (356 nm, 440 nm, 587 nm). Results showed that, after irradiation for 2 h, the photo-reduction rate of Cr(VI) (pH = 2.82) for TiO₂(450 nm) was 96%, exhibiting an increase of 5% and 8% compared with TiO₂(370 nm) and TiO₂(600 nm) ^[22]. Ananpattarachai et. al. synthesized a novel bio-catalyst by adding TiO₂ in chitosan/xylan with both adsorption and reduction capacity

under ultraviolet irradiation, which achieved photocatalytic reduction rate of Cr(VI) at 0.56×10^3 ppm-min^[23]. Li combined graphene and TiO₂ nanospheres to facilitate photocatalytic reduction of Cr(VI) under UV irradiation^[24].

However, Wang et. al. pointed out that the application of TiO₂ is limited due to its disadvantages like low photocurrent quantum yield, low solar energy utilization efficiency, difficult post-separation after treatment, and agglomeration. Great efforts have been devoted to searching for new visible-light active photocatalysts. Metal-organic frameworks (MOFs), a newly emerged type of functional inorganic-organic hybrid materials, were sought. MOFs can facilitate the fast transport and good accommodation of targeted molecules due to their desirable topology and high surface area^[25]. Especially, the MOFs' band gap is closely related to the HOMO-LUMO gap, and energy transfer can take place from the organic linker to the metal-oxo cluster within some MOFs under light irradiation^[26], which can be further tuned to achieve efficient light harvest via rational modification of the inorganic unit or organic linkers^[27]. In previous researches, some typical MOFs (or their composites) were employed as photocatalysts for the reduction of Cr(VI) under visible light irradiation, including MIL-101(Fe), ZnO@ZIF-8, Pd@UiO-66(NH₂), HPMo@MIL-100(Fe) and so on, with excellent reduction efficiency (100%)^[11].

Adsorption

Adsorption is always attractive and the most promising for Cr removal though generating non negligible amounts of sludge. To date, a variety of materials have been tried as adsorbents for Cr (VI) removal. The newly modified adsorbents were usually characterized by Fourier-transform infrared spectrophotometer (FTIR), scanning electron microscopic analysis (SEM)^[18, 19], transmission electron microscopy (TEM) and X-ray diffraction (XRD)^[28]. Besides, pseudo-second-order kinetic model and Langmuir isotherm model provided better correlation for the adsorption of Cr on the studied adsorbents^[17, 18, 19].

The raw material of adsorbent varies including organic, inorganic and also their combination. Polyaniline (PANI) coated magnetic Fe₃O₄, carbon fabric and cellulose composites was found to improve both the removal rates and removal capacity of Cr(VI)^[17]. Lee et. al. applied Fe₂O₃-carbon foam for Cr removal, which exhibited 6.7 mg/g adsorption capacity^[29]. Mesoporous carbon microspheres (MCMs) possessed excellent adsorption capacity for Cr at as high as 165.3 mg/L, while Fe₃O₄-loaded MCMs was at 156.3 mg/L. What is more, Fe₃O₄-loaded MCMs had a good regeneration ability with a capacity of 123.9 mg/L for the fifth adsorption-desorption cycle^[30].

As biomass waste are discarded in large amount and have potential absorption capacity at low cost, researchers spend time in studying their Cr-removal efficiency. The biosorbent from modified Litchi peel showed maximum adsorption at 9.55 mg/g at 303 K^[31]. Acrylonitrile grafted banana peels greatly improve the adsorption capacity at 96%. The optimum conditions for adsorption of Cr(VI) was pH 3, adsorbent dose 4 g/L, concentration 400 mg/L and contact time of 120 min^[32]. Results also showed that removing of peptic and viscous compounds, and the incorporation of a side chain (—CH₂—CH—C=N) play crucial role in the enhancement of removal capacity^[32]. Groundnut hull was also considered as potential biosorbent in Owalude's study^[33]. Chitosan with quaternary ammonium groups was the other kind of biosorbent with excellent adsorption capacity at 39.1 mg/L^[34]. Amine and quaternary ammonium groups are considered to be the main sites for sorption through electrostatic interaction, ionexchange, or a combination of these two mechanism^[35]. Chug

even found that extracellular polymeric substances (EPS) produced by two bacteria *Azotobacter beifreinetii* and *Bacillus subtilis* could remove Cr(VI) from aqueous system. In the adsorption process, carboxyl and phosphate groups were involved [36].

A breakthrough in the field is the resort to adsorbents with both reductive and sorption properties in a single solid [4]. Zaitseva et. al. synthesized a bi-functional silica adsorbents for Cr(VI) reduction by thiol groups (SH) and subsequent complexation of Cr(III) by ethylenediaminetriacetate groups (ED3A). The most appropriate pH range was 1-3 and good Cr removal performance was observed in the presence of interference like ionic strength and other heavy metals [4]. Kuppusamy confirmed that the utilization of dried twigs of *Melaleuca diosmifolia* without pretreatment can detoxify and remove Cr(VI). This biosorbent constituted high concentrations of reducing compounds for Cr(VI) reduction. Especially, this biosorbent can treat Cr(VI) at wide-ranging pH (2-10) and temperature (24-48 °C) with high removal efficiency [18]. In Fellenz's study, the amino-functionalized MCM-41 sorbents exhibited both adsorption and reduction ability. The partially reduction theory was proposed that a proton released from the solid surface to the solution, afterwards, Cr(III) was partially retained onto the samples surface due to the Lewis basicity of the nitrogen atoms [37]. In Zhu's research, Nitrogen and Fe(III) were co-doped in chitosan to improve the amphoteric adsorption performance. Interestingly, as coexistent Cu(II) and Cr(VI), it was found that Cr(VI) induced H⁺ consumption and shielding effect to improve Cu(II) adsorption, while Cu(II) attracted Cr(VI) as cation-bridge and replace H⁺ to enhance Cr(VI) redox [38].

Application of nanotechnology

TiO₂, ZnO, Fe₃O₄ and zero-valent iron are most widely used in Cr(VI) removal in aqueous solution. The application of nanotechnology also enhance the Cr(VI) removal performance. Compared with traditional TiO₂, Chen et. al. synthesized a highly reductive TiO₂ nanocrystals on which diethylene glycol (DEG) chemically bonded. The newly synthesized TiO₂ catalyst possessed a strong internal hole-scavenging effect and a high electron-releasing capacity. Besides, it had a good longevity for multiple use [20]. Deng et. al. successfully prepared a phosphorus doped porous ultrathin carbon nitride nanosheets (PCN-S) for Cr(VI) removal. Results showed that large specific surface areas from the porous nanosheet structure provided quantities of active sites for the photocatalytic reaction. As for the low solar energy utilization efficiency of traditional TiO₂, visible-light-driven (VLD) CoO_x loaded TiO₂-based nanosheets (Co-TNSs) with surface-enriched CoO_x nanoparticles were synthesized with success. It was found that loaded CoO_x nanoparticles considerably enhance the visible-light (VL) absorption and a red-shift of the band gap of the TNSs. Also, the appropriate amount of CoO_x (2.5 at.%) loading can effectively inhibit the recombination of photo-generated electron-hole pairs, thus improve the separation efficiency of charge carriers [16].

The application of zero-valent iron nanoparticles in Cr(VI) removal is mainly on the basis of reduction from Cr(VI) to Cr(III). In Yu's case, it was found that higher pH values resulted in higher Cr(VI) removal efficiencies, which was because more OH⁻ ions were generated when more Cr(VI) was reduced to Cr(III) by the nano zero-valent (nZVI) iron particle [21]. As the efficiency of zero-valent iron nanoparticles (ZVINS) for the Cr(VI) removal was strongly decrease due to particle agglomeration, Esfahani et. al. made a sepiolite-stabilized ZVIN composite to solve this problem. They found that the removal efficiency increased in acidic and neutral pH conditions, while it considerably decreased by increasing the Cr(VI) concentration [9]. Fu et. al. also newly synthesized a humus-supported nanoscale zero-valent (H-NZVI) with both concurrent physical adsorption and

chemical reduction for Cr(VI) removal. It was showed that supported NZVI in humus has succeeded in preventing aggregation and oxidation ^[39]. Also, the presence of bentonite could decrease the aggregation of nZVI and increase its reactivity ^[40, 41].

Compared with other Cr(VI) removal techniques, adsorption is often superior since it is cost effective, easy handling, flexible and selective. They can also be stripped and recycled. Researcher still showed keen interest in improved and advanced adsorbents with high surface areas and sorption capacities ^[1]. Nanosorbents are sought in forms of particle, sphere, sheet, tube, fiber and composite. The Cr(VI) adsorption capacity of various newly nanoadsorbent are shown in Table 1. In the nanoadsorbent studies, solution pH, contact time, adsorbent dose and initial metal concentration were investigated. It was found that initial concentration has only a very little effect on adsorption ^[42]. With increase in pH, the removal efficiency decreases, as the surface of magnetite nanoparticles become more negatively charged, resulting from repulsion between Cr(VI) and magnetite nanoparticles. The adsorbent dosage increases can enhance the removal efficiency to the maximum, however, it decrease afterwards also with the existence of aggregation ^[42]. Regarding to the effect of time, the removal efficiency increased to the maximum and reach equilibrium ^[42]. Talreja et. al. used the Fe nanoparticle (NP)-containing carbon nanofibers (CNFs) grown on porous carbon microbeads (~0.5mm) as adsorbent. Differently, Cr-laden wastewater could be effectively treated with this nanoadsorbent without adjusting the pH in a pretreatment step. The mechanism of the removal was suggested to be both physisorption and electrostatic interactions ^[43]. Desorption and reuse of the nanoadsorbent is of great important. Rajput et. al. stripped the nanoparticles with 20mL of 0.01M NaOH by agitating at 25°C for 30 min. The percent desorption was ~44% ^[1]. Choudhury et. al. regenerated nanoadsorbent using 50ml 0.1M NaOH by stirring 90min, and finally obtained maximum 75% desorption. Increasing desorption cycle resulted in lack of active sites and them decrease the performance of nanocomposite. But after 4th sorption cycle, it showed significant removal efficiency of 60% ^[44]. Chitosan-1,2-Cyclohexylenedinitrilotetraacetic acid - graphene oxide (Cs/CDTA/GO) could be regenerated more than three times based on its adsorption/desorption cycles. After that, the removal efficiency was more than 95% ^[45]. For the threonine doped polypyrrole nanocomposite, the removal efficiency remains unchanged for the first four cycles and was above 97% but the removal efficiency was reduced to 69% and 40% in the following fifth and sixth cycles respectively.

Table 1 Langmuir adsorption capacities for Cr(VI) removal of various kinds of nanoadsorbent

Nanoadsorbent	Adsorption capacity [mg/g]	Reference
Magnetite (Fe ₃ O ₄) nanoparticles	20.2 (25 °C) 26.8 (35 °C) 34.87 (45 °C)	1
Mesoporous magnetite (Fe ₃ O ₄) nanospheres	6.64 (25 °C) 7.31 (35 °C) 8.90 (45 °C)	46
Humus-supported nanoscale zero-valent iron	40.4	39
Bentonite-supported nanoscale zero-valent iron	45 (0.001M ionic strength) 60.50 (0.01M ionic strength) 66 (0.05M ionic strength)	41
Fe-grown carbon nanofibers containing porous carbon microbeads	41	43
Biogenic iron based nanoparticles	983.2 mg Cr(VI)/g Fe	47
Titania embedded dead yeast nanocomposite	162.07	44
Carbon nanotubes supported by activated carbon	9.0	48
Reticulated chitosan micro/nanoparticles	68.9 (25°C, pH4) 12.4 (25°C, pH2)	49
Chitosan	25 (25°C, pH4)	49
Chitosan-CDTA-GO nanocomposite	166.98	45
Threonine doped polypyrrole nanocomposite	185.5	50

Conclusions

Environmental regulations have become more stringent in the past two decades, requiring an improved quality of treated effluent. A wide range of treatment technologies such as chemical precipitation, coagulation-flocculation, ion exchange and membrane filtration, have been developed and widely used for Cr(VI) removal. To date, researchers showed greater interest in membrane electrolysis, photocatalytic reduction and adsorption. Nanotechnology as novel methods have integrated in photocatalytic reduction and adsorption by nanomaterial, and have made good progresses in cost-effective, technical-applicable, and plant-simple methods for Cr(VI) removal. Liquid membrane combined with electrodialysis is now in the progress. Photocatalytic reduction with TiO₂ is popular, however, disadvantage like difficult post-separation after treatment, and agglomeration limit its application. Future work need to examine the separation of TiO₂, e.g. by making the synthesized TiO₂ catalyst magnetic and separating it by a magnetic field ^[049]. MOFs was found to be the alternative as photocatalyst. Adsorption was considered as the promising method for removal. The adsorbents are made from natural and synthesized organic, inorganic and the combination of them in order to seek for a low-cost and effective adsorbent. Nanoadsorbents with large surface area are popular nowadays, but the agglomeration of nanoadsorbents still needs further study so as to enhance the removal efficiency, e.g. through coated with other material like humus and bentonite.

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