A novel chitosan functional gel included with multiwall carbon nanotube and substituted polyaniline as adsorbent for efficient removal of chromium ion

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HIGHLIGHTS

- A new chitosan based multicomponent functional gel (FG) was synthesized.
- The functional capacity of the FG to remove chromium(VI) was explored.
- Synergies among the four components in FG leads to excellent adsorption efficiency.
- FG exhibits excellent adsorption efficiency, reusability, and regeneration.
- A plausible mechanism for chromium removal by the FG is suggested.

GRAPHICAL ABSTRACT
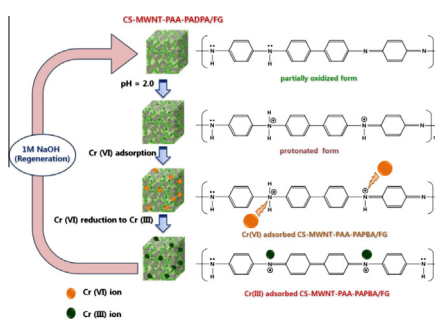
ABSTRACT

The efficacy of a new chitosan (CS) based functional gel (FG), comprising multiwall carbon nanotube (MWNT)–poly(acrylic acid) (PAA)–poly(4-amino diphenyl amine) (PADPA), was investigated towards removal of hexavalent chromium (Cr(VI)). The new FG (CS–MWNT–PAA–PADPA/FG) was synthesized by free radical polymerization and cross-linking reactions. Characterization of the gel was done by Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis, X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy. Pore parameters of the gel were evaluated by mercury porosimetry. Batch adsorption experiments were conducted to evaluate the FG for the removal of Cr(VI) from synthetic as well as field samples. The maximum Cr(VI) adsorption capacity was achieved for CS–MWNT–PAA–PADPA/FG owing to the synergistic effects from the individual components. The individual component such as (MWNT, CS, PAA and PADPA) in CS–MWNT–PAA–PADPA/FG plays a vital role to the improvement in Cr(VI) adsorption/removal. CS and PADPA were the nucleus for Cr(VI) adsorption through binding with –NH$_2$ sites. PAA provides internal H$^+$ ions within the gel and increases the adsorption efficiency of CS–MWNT–PAA–PADPA/FG over a wider pHs. PADPA provides additional –NH$_2$ sites over CS for Cr(VI) adsorption. CS and PAA endow three dimensional hydrogel framework and controls the swelling/shrinking action of the hydrogel. MWNTs impart stability to the gel during adsorption–desorption cycle and improves re-useability. The Cr(VI) removal mechanism was investigated by FTIR spectroscopy, X-ray absorption spectroscopy and XPS. The results suggest complexation interactions

between the multiple organic functional groups in FG and Cr(VI) and transformation of Cr(VI) to Cr(III). Furthermore, the new CS–MWNT–PAA–PADPA/FG is stable and recyclable, retaining about 85% of the removal efficiency up to three adsorption cycles.

1. Introduction

Heavy metals, such as chromium (Cr), mercury and cadmium, enter into the environment and cause health hazard due to their toxicity and bioaccumulation in the human body. The hexavalent state (Cr(VI)) is classified as a carcinogen by the International Agency for Research on Cancer, due to strong mutagenic and teratogenic properties [1]. The US Environmental Protection Agency regulations set the maximum total Cr content in drinking water as 0.1 mg/L or 100 ppb [2]. Besides, Cr(VI) are highly soluble and mobile in aquatic system and often discharged into the environment at levels well above the regulatory trace limits leading to negative impacts on plants, animals and human health [3]. A variety of conventional techniques has been developed for the removal of Cr(VI) including chemical precipitation, chemical/electrochemical reduction, ion-exchange, membrane separation and solvent extraction. Adsorption technologies have been investigated for Cr(VI) removal in fundamental research as well as industrial settings. High adsorption capacities, operational convenience, versatility and the range of compounds available all encourage adsorption technique for Cr(VI) removal.

A number of carbonaceous adsorbents such as activated carbon [4] have been tested because of their low cost and resistant to corrosion. Nanocarbonaceous materials have also been tried as adsorbent due to their high surface area and adsorption capacity [5]. Multiwalled carbon nanotubes (MWNTs) were recognized as the efficient adsorbent for the removal of organic and inorganic contaminants, either in their oxidized form [6] or in conjunction with magnetic materials [7,8]. Also, graphene based multifunctional materials have been utilized for the removal of few of the environmental contaminants [9–14]. Unfortunately, filtration and centrifugations times associated with carbonaceous compounds are excessive, resulting in loss of adsorbents. Furthermore, separation becomes a critical issue in the case of small particles. Besides few of the drawbacks, such as ineffective reduction of Cr(VI), regeneration of adsorbent and disposal of the Cr(VI) sludge plus procedural complexity and high operating cost, which were reported in existing methods for the removal of Cr(VI), need to be circumvented [15,16,4]. Therefore, there is still a requirement for the development of an efficient adsorbent having high adsorption capacity for Cr(VI) removal. Preferably, it would be more advantageous if the Cr(VI) removal is assisted with simultaneous reduction of adsorbed Cr(VI).

Hydrogel based systems hold the potential for effective heavy metal removal and received increased attention relative to conventional counterparts [17]. Adsorbing gels usually have well defined porous structures and chemically responsive functional groups. The latter may include carboxylic acid, amine, hydroxyl, or sulfonic acid moieties. The functional groups in the gels can form complexes with toxic metal ions and improve adsorption efficiency [18]. However, hydrogels generally lack selectivity as they can bind several types of metal ions without high selectivity for a specific metal ion. Only limited studies have addressed the potential for specificity of heavy metal removal using specific functional-group containing hydrogels (FG) [19]. FGs constitute effective adsorbents because individual metal ions are chemically bonded by the specific functional groups/components in them. Such functional

groups can be introduced into the FGs using copolymerization, grafting and also interpenetrating polymer network (IPN) formation [20,21]. Importantly, the composition of IPN-based FGs can be tailored through targeted design in order to develop efficient adsorbents for specific metal ion.

Recently, synthetic polymer based hydrogels such as poly acrylic acid (PAA) and polyacryl amide hydrogels, were synthesized and such hydrogels demonstrated good adsorption capacity as effective adsorbent for various contaminants [22,23]. It has been reported that inclusion of nanoadditives such as MWNTs could improve the adsorption capacity of the polymeric hydrogels [24,25]. The included nanoadditives may function as dispersing agent to increase the interconnected porous structure of polymeric composite gels [26,27]. In the hydrogel based adsorbents, MWNTs have also been used as reinforcing and filling agents, to enhance the mechanical properties of hydrogels [28,29]. It has also been demonstrated that the added nanocomponent could not only improve the loading capacity but also shorten the adsorption time [30]. However, the high cost fabrication process, complex steps needed for the incorporation of nanocomponent, lack of specific functional groups in the hydrogels for binding the analyte and use of non-environment friendly polymers may limit the application of the polymeric composite hydrogels from application as low-cost, fast and efficient adsorbent. In this work, our main focus is to develop an efficient chitosan (CS) based FG adsorbent incorporated with a nanocomponent (MWNT) and functional polymers to improve the Cr(VI) removal efficiency.

CS is an excellent bioadsorbent and has often been applied in the treatment of organic pollutants, including heavy metals in aqueous environmental systems [31]. The chemical structure of CS is shown in Scheme 1. Poly(1 → 4)-2-amino-2-deoxy-ᴅ-glucose units are present along with a high content of hydroxyl and amine groups [32]. It has been in fact demonstrated that unmodified CS exhibits poor adsorption efficiency for Cr(VI). The three dimensionally ordered structures of CS have restricted ability for metal ion adsorption because of the limited preferential adsorption of metal ions by the amorphous region of the CS. On the other hand, the hydrogel form of CS could have improved adsorption capacity by reducing the crystallinity of CS. However, uptake of the metal ion by CS was improved through cross-linking with other polymers [33]. Few studies have also been reported on CS based gel systems [34–36]. The studies indicate that CS hydrogels are capable of improving adsorption capacity. However, it should be noted, that the poor acidic resistance and mechanical strength limit the application of pristine CS hydrogel as the adsorbent. It would be possible to incorporate additional/new functional groups within CS based materials in order to (i) strengthen the binding, (ii) increase the number of adsorption sites, (iii) change the pH range for metal sorption and/or (iv) alter the sorption selectivity for targeted trace metals. Besides, the acid resistance and mechanical stability can be improved with judicious selection of additives for the CS based gel.

In the present work, the adsorption efficiency, acidic resistance, selectivity toward Cr(VI) and mechanical strength of CS are improved by including amine-containing PANI type polymer chains, PAA and MWNTs, respectively, as well through the formation of IPN structure between them. PANI, an amine-based conducting polymer, has earlier been exploited for efficient metal