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Nano-Bio sequential removal of hexavalent chromium using polymer-nZVI composite film and sulfate reducing bacteria under anaerobic condition

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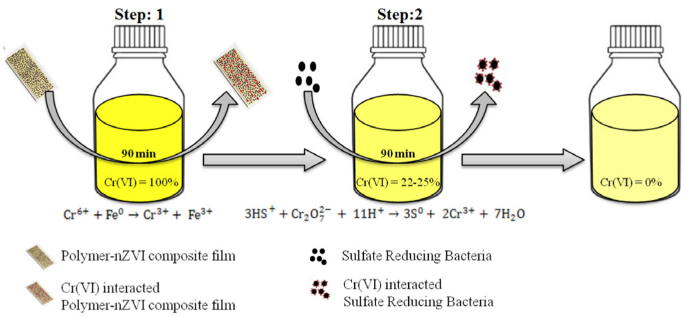
HIGHLIGHTS

- The first approach to use sequential nano-bio process to remove Cr(VI) under anaerobic conditions.
- Initially (i) nZVI composite treatment, and (ii) sequential usage of sulfate reducing bacteria.
- nZVI composite film prepared by layer by layer method using chitosan/PEG blend.
- Sequential process tested with environmental water samples.

GRAPHICAL ABSTRACT



Step1: Cr(VI) removed using nZVI composite film and the nZVI composite film was removed after saturation.
Step2: The left out Cr(VI) was removed using Cr(VI) adapted Sulfate reducing bacteria

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ABSTRACT

A sequential method for removing Cr(VI) was studied using polymer-nano zero valent iron (nZVI)-based composite film and live biomass of sulfate reducing bacteria (SRB) under anaerobic conditions. The polymer-nZVI composite film was made using layer-by-layer coating of chitosan, polyethylene glycol (PEG) blend, poly (sodium 4-styrene sulphonate) solution (PSS), and nZVI on a glass slide. The conditions for the removal of Cr(VI) through polymer-nZVI nanocomposite film were optimized using Response Surface Methodology (RSM). SRB was grown in Baar's medium was adapted to 10 mg L^{-1} of Cr(VI) and the live biomass obtained thereof was used for removal of Cr(VI). Cr(VI) removal capacity of 394 mg g^{-1} was observed at optimal conditions by nano-bio sequential removal process using polymer-nZVI-based composite film and SRB. The XRD, SEM-EDX, and FT-IR spectral data demonstrated the reduction of Cr(VI) and binding of chromium (Cr) species on the polymer-nZVI-based composite film and SRB biomass. The applicability of the sequential

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Cr(VI) removal process using polymer-nZVI-based composite film and SRB was successfully verified in Cr(VI)-spiked environmental water samples.

1. Introduction

Chromium is extensively used in industries like metal industry, wood preserving industry, and pigment production industry (Ravikumar et al., 2016b). The use of chromium in industries is increasing drastically leading to consequent increase in pollution (Rashmi et al., 2013). Increasing chromium in wastewaters can adversely affect biota (Allan and Kukacka, 1995; Ravikumar et al., 2016a). Hexavalent chromium has more toxicity than trivalent chromium because high water solubility and mobility (Baral and Engelken, 2002). According to the US Environment Protection Agency (EPA), by limiting the concentration of total chromium in drinking and surface water is fixed at 0.1 mg L^{-1} (USEPA, 2012). Food and Agriculture Organization (FAO) has given the same limit for chromium (0.1 mg L^{-1}) in crop production area (Mousavi et al., 2013). Hence, the removal of hexavalent chromium from the environmental water is essential, and this necessitates the development of simple, eco-friendly techniques for Cr(VI) remediation.

To comply this Cr(VI) removal from waste water there are various physical methods that include ion-exchange, membrane filtration and adsorption. Among these methods, adsorption methods have significant advantages over the other techniques because of its simple design, ease of operations, cost effectiveness, and recycle ability and ability to reduce Cr(VI) concentration below the acceptable level from huge amount of environmental water (Bhaumik et al., 2016).

In the past few years, nZVI is extensively used for removing contaminants like heavy metal [Cr(VI)] by precipitation (Cao and Zhang, 2006) and nitrates by reduction (Wang et al., 2006). nZVI has several advantages over ZVI which includes smaller particle size, large specific surface area, higher density of reactive sites, faster and complete reactions and high reduction capacity (Dong et al., 2017). These properties significantly enhance the contaminant degradation reactions. Also, nZVI has the capability of injecting directly into a contaminated aquifer (Jang et al., 2014). Therefore, the nZVI is widely used and well established for the removal of Cr(VI) in environmental applications (Mueller et al., 2012). Selected previous studies on Cr(VI) removal using nZVI based composites are mentioned in Table S1, in supplementary information.

Biopolymers such as chitosan and cellulose form another category of materials used widely for contaminant removal from water (Wang et al., 2010). Chitosan is generally used in the form of films and microspheres as possible adsorbents of chromium from water (Paul et al., 2014). Chitosan when mixed with polyethylene glycol (PEG) could improve the chemical stability and other properties for the sorbents (Sağ and Aktay, 2002).

Microbial remediation is often used to remove chromium from waste water. It has been reported that among microbial communities, SRB was known to be highly tolerant bacteria (such as *Desulfovibrio desulfuricans* hereafter referred as SRB), that can be used for removal Cr(VI)from water (Ahmadi et al., 2016; Fude et al., 1994). SO_4^{-2} can be reduced by anaerobic sulfate reducing bacteria. Sulfate reducing bacteria uses SO_4^{-2} as a part of their electron acceptor and gives the final product as hydrogen sulfide (Kumar et al., 2017). This hydrogen sulfide reacts with heavy metal such as chromium to produce metal sulfide. Waste water containing Cr(VI) can be treated with the help of SRB bacteria and SRB grown separately. The biogenic product formed by the SRB bacteria by reducing SO_4^{-2} then it is introduced to the Cr(VI) (Kim et al., 2001).

There are no previous reports on integrating nano-biotechnological processes for remediating Cr(VI) in environmental water samples. Nano scale zero valent iron has been widely been used for the reductive removal of heavy metals, though there has been persistent concerns about environmental/ecological impact of the particles. The usage of microbes for Cr(VI) remediation has always had numerous advantages as it is an eco-friendly technology. Previous studies have used nZVI with different supporting materials for Cr(VI) such as chitosan beads, biochar, bentonite and graphene sheet (Dong et al., 2017; Li et al., 2016; Liu et al., 2010; Shi et al., 2011).

To our knowledge this is the first approach to use a two step nano-bio process to remediate Cr(VI) under anaerobic conditions-(i) nZVI composite treatment, and (ii) sequential usage of sulfate reducing bacteria *Desulfovibrio desulfuricans*. The composite film is prepared through layer-by-layer method on the glass slide coated with chitosan/PEG blend, over which PSS (poly sodium 4-styrene sulphonate) and nZVI were added to increase the binding of Cr(VI) by enhancing the positive charge density on the film surface (Paul et al., 2014). Immobilization of the nZVI on chitosan/PEG layer was done to avoid aggregation. PSS supports electrostatic hybridization between poly cationic chitosan and positively charged nZVI. Mechanical stability was provided with the help of glass film. Experiment was performed in the anaerobic condition to increase the efficiency of Cr(VI) removal. After the chitosan film interaction, anaerobic SRB bacteria was used to remove further Cr(VI).

2. Materials and methods

2.1. Chemicals

Sodium borohydride ($NaBH_4$) and 1,5 di- phenylcarbazide were obtained from SD Fine Chemicals, Mumbai, India. Ferrous sulfate ($FeSO_4$. $7H_2O$) and EDTA ($C_{10}H_{14}N_2Na_2O_8$. $2H_2O$) were purchased from Sisco Research Laboratories Pvt.