



Simultaneous removal of trichloroethylene and hexavalent chromium by green synthesized agarose-Fe nanoparticles hydrogel



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HIGHLIGHTS

- Agarose-Fe NPs hydrogel were produced via two green steps.
- Both Cr(VI) and TCE were removed by agarose-Fe NPs hydrogel.
- 84.9% of Cr(VI) and 93.8% of TCE were simultaneously removed.
- Chemical reduction played a role in the removal of both Cr(VI) and TCE.

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ABSTRACT

The development of highly efficient, eco-friendly and cost-effective remediation technology to remove mixed contaminants is now in progress. Here, agarose-Fe nanoparticles (NPs) hydrogel were produced via two green steps to remove mixed contaminants, specifically trichloroethylene (TCE) and hexavalent chromium (Cr(VI)). Approx. 84.9% of Cr(VI) and 93.8% of TCE were simultaneously removed over 24 h in their co-existing solution, while 94.1% of Cr(VI) and 97.2% of TCE were separately removed by agarose-Fe NPs hydrogel. Scanning Electron Microscopy (SEM) suggested that the macroporosity of agarose-Fe NPs hydrogel facilitated the mass transfer between agarose-Fe NPs hydrogels and mixed contaminants, and that Fe NPs were uniformly immobilized into the hydrogel. X-ray Photoelectron Spectroscopy (XPS) and Fourier Transform Infrared Spectroscopy (FTIR) provided evidence supporting the co-removal mechanism. XPS result indicated that: (1) chemical reduction played a role in the removal of both Cr(VI) and TCE; and (2) iron oxides and Fe(III)-Cr(III) complexes might be formed after reaction. FTIR result showed that some functional groups were involved in the removal process. Moreover, the presence of iron oxides were confirmed by FTIR. Both SEM and XPS results verified that encapsulation could describe such immobilization of Fe NPs using agarose. Finally, the kinetics study supported the removal mechanism. Such encapsulation of Fe NPs via a green strategy is simple, quick, and cost-effective, making *in situ* remediation of mixed contaminants more favorable.

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1. Introduction

Rapid industrialization has led to many contaminants entering terrestrial and aquatic environments, and consequently this has posed serious environmental concerns. Water pollution is a particularly serious problem because many contaminants exceeding recommended maximum contaminant levels are directly or indirectly discharged into aquatic systems without appropriate disposal procedures, thus contaminating water quality. So far, various contaminants have been detected in groundwater and surface water systems, many of which can adversely influence hydrology, ecol-

ogy, and human health [1]. Generally, these contaminants can be divided into two categories: organic and inorganic contaminants. Organic contaminants usually include chlorinated solvents, petroleum hydrocarbons, pesticides, volatile organic compounds (VOCs), and polycyclic aromatic hydrocarbons (PAHs). These organic contaminants are normally classified as flammable, hazardous, and carcinogenic materials [2]. Inorganic contaminants primarily contain nutrients (nitrate and phosphate), ammonia, halides, acids, and heavy metals (e.g., chromium, lead, cadmium zinc, mercury, and arsenic).

Of these contaminants, trichloroethylene (TCE) is a well-known carcinogenic and mutagenic halogenated VOC with 5 µg/L maximum contamination level allowed in drinking water [3]. Generally, TCE is introduced into aquatic systems through discharges from

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industrial processes such as textile processing, refrigeration, lubricants, and adhesives [4]. Given its toxic impact, several biological, chemical, and physical methods have already been proposed for removing TCE [5–9]. Heavy metals are among the most common inorganic contaminants, most of them are highly toxic and harmful to animals and human beings, even at low concentrations. Some of them can be assimilated, stored, and concentrated by organisms [10]. Chromium extensively used in tanning, electroplating, and textile dyeing is of particular environmental concern in the aquatic system, which normally exists in two stable states: trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)). Cr(III) is less toxic and has low solubility in aquifers while Cr(VI) is a well-known highly toxic, carcinogenic, mutagenic, and teratogenic mobile ion in the environment [11]. Considering these properties, Cr(VI) must be physically or chemically removed from contaminated water before being discharged into the aquatic system. Several technologies such as chemical precipitation, membrane separation, ion exchange, reverse osmosis, and electrodialysis [12,13], have attempted to remove Cr(VI) from aquatic systems.

It is well-known that more than one type of contaminant exists in wastewater or contaminated groundwater, and that some organic compounds derived from petroleum and organic chemical industries contain metal additives [14]. Therefore, the co-existing of organic compounds and heavy metals in wastewater is a serious issue. However, most removal processes are designed for treating only one specific contaminant in current applications. To the best of our knowledge, only a few reports have investigated the simultaneous removal of organic and inorganic contaminants [1,2,15,16]. These studies have proved useful in examining the removal of mixed contaminants but some drawbacks have emerged in these methods, for example high cost, inefficiency, and generating toxic sludge [2]. Consequently, it is still necessary and urgent to develop alternative methods that are cost-effective, efficient, and meeting the environmental requirements. As a novel tool with excellent properties (i.e. easy accessibility and high removal efficiency), Fe-based nanoparticles (NPs) have received extensive attention in the disposal of contaminated water and soils. A wide range of contaminants, for instance, heavy metals, azo dyes, nitrate, chlorinated organic compounds, and nitroaromatic compounds, have been separately removed by Fe-based NPs [17–19]. One recent promising advance is represented by chitosan stabilized bimetallic Fe/Ni NPs simultaneously removing amoxicillin and Cd(II) from aqueous solution [20]. The result revealed that reducing amoxicillin and adsorption of Cd(II) were co-presented, suggesting Fe-based NPs have the potential to simultaneously remove mixed contaminants from wastewater. However, only a few reports have been published on removing mixed contaminants using this promising technology and green synthesized Fe-based NPs have not been used for removal of mixed contaminants.

As an eco-friendly and cost-effective strategy, treating Fe precursor with plant extracts has attracted attention to the synthesis of Fe-based NPs [21,22]. In our previous reports, grape leaf extract was successfully utilized to synthesize Fe-based NPs [23,24]. In our subsequent work, we focused on the immobilization of green synthesized Fe NPs using agarose in the form of hydrogel (agarose-Fe NPs hydrogel), where both Fe NPs and agarose-Fe NPs hydrogel were prepared via the green method. Several remarkable advantages were displayed. Firstly, using grape leaf not only produced cost-effective Fe NPs applied to environmental remediation but also reduced the environmental impact of grape leaf, principally avoiding the use of expensive and toxic chemicals as reducing and capping agents in the synthesis of Fe NPs [25]. Secondly, agarose, which derives from red–purple seaweeds, is a neutral polysaccharide. Its solution can form thermal hydrogels when cooled down below its generation temperature (31–36 °C). By cooling a

hot solution of agarose in water, a 3D network was formed through hydrogen bonding and hydrophobic interactions. Previous reports have demonstrated that such hydrogel can be widely used for biomedical applications owing to its bio-similarity, aqueous inner environment, porous structure, and ability to conjugate with various biological macromolecules [26]. Moreover, agarose hydrogel is nontoxic, inert, biodegradable, cost-effective and biocompatible, which meets the principles of green chemistry. As compared to other reported immobilization technologies using matrix materials like alginate or chitosan, the formation of agarose hydrogel utilized liquid nitrogen rather than chemical agent like sodium hydroxide, therefore this process was quicker (a few minutes) and more eco-friendly. Besides, encapsulation has been proved to describe such immobilization of Fe NPs using agarose. Of these immobilization technologies, encapsulation is expected to be better in facilitating reaction between contaminants and the encapsulated nanoparticles [26]. Thirdly, Fe NPs easily agglomerate in water to form larger aggregates owing to magnetic and van der Waals forces or tend to react with air, contributing to the significant loss of reactivity. However, Fe NPs are more stable in the form of agarose-Fe NPs hydrogel because the adverse impacts emanating from agglomeration and oxidation are mostly overcome. Fourthly, it is easy to recycle agarose-Fe NPs hydrogel rather than dispersed Fe NPs from wastewater. Such a synthesis process was simple, quick, eco-friendly, and cost-effective, enabling such material to exhibit a relatively high market value in environmental remediation. However, it is still unclear how it works when removing mixed contaminants because their removal remains a challenge [18]. Therefore, we reported the simultaneous removal of TCE and Cr(VI), which are typical targets of organic and inorganic contaminants, using agarose-Fe NPs hydrogel. To clearly identify the removal mechanism, X-ray Photoelectron Spectroscopy (XPS) and Fourier Transform Infrared Spectroscopy (FTIR) were employed to provide the evidence.

2. Experimental

2.1. Materials and chemicals

Ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), TCE, potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), and agarose were purchased from Sigma–Aldrich Co. (Australia), and all of them were analytical grade. Deionized water ($\text{pH} = 5.8 \pm 0.2$) obtained from Milli-Q Elga System was utilized in all experiments.

2.2. Synthesis of Fe NPs and agarose-Fe NPs hydrogel

As described in our previous study [27], the grape leaf extract was prepared by adding 2.0 g of finely ground grape leaf powder in 50 mL of water at 100 °C for one hour, and filtered through a 0.45 μm polytetrafluoroethylene (PTFE) filter. To synthesize Fe NPs, the same volume of Fe^{2+} solution (0.01 mol/L) and grape leaf aqueous extract was mixed thoroughly with a stirrer at room temperature for 30 min. The formation of Fe NPs was marked by the immediate appearance of intense black precipitate. Fe NPs were dried using a freeze dryer and then retained in a vacuum system prior to use.

To obtain agarose-Fe NPs hydrogel, heating the agarose solution which was prepared by adding 0.075 g of agarose into 6 mL of water until agarose was completely dissolved at melting point (65–85 °C) using the stirrer. Then, 0.080 g of Fe NPs was added to the hot agarose solution, and the mixture was stirred for another several minutes to ensure homogeneity. The agarose-Fe NPs solution was dropped into the liquid nitrogen by pipette tip when hot, and the agarose-Fe NPs hydrogels were formed immediately.

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