



## Porous stainless steel supported magnetite crystalline membranes for hexavalent chromium removal from aqueous solutions

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### ABSTRACT

Magnetite (Fe<sub>3</sub>O<sub>4</sub>) crystalline membranes were prepared on a porous stainless steel support by a sol–gel method for the sake of hexavalent chromium [Cr (VI)] removal from aqueous solution. The impact of the fabrication parameters including concentrations of casting solutions, multiple coatings, sintering atmospheres and temperatures, as well as heating ramp rates was studied. The morphologies were characterized by scanning electron microscopy and Cr (VI) concentration was determined by spectrophotometry. Planar and continuous membrane was obtained when fired initially in air followed with N<sub>2</sub> and the air–nitrogen changing temperature was 400 °C. The membrane consisted of small cubic grains when the casting solution was 0.032 mol/L and the thickness was ~5 μm. When the concentration was 0.065 mol/L, the membrane was composed of small cubic grains at the bottom and big pillar ones on the top and the thickness increased to ~25 μm. Repeated coatings had no significant impact on the morphologies and thicknesses of the resultant membranes. When fired at 850 °C, pure magnetite membranes with clear cubic grains at the bottom and clear pillar ones on the top were obtained. Pillar grains can be obtained when sintered at a heating ramp rate of 1 °C/min. The Cr (VI) removal test exhibited an elimination efficiency of 92.5%, indicating a promising application to remove Cr (VI) from aqueous solution.

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### 1. Introduction

The contamination of drinking water by hexavalent chromium [Cr (VI)] has been drawing great attention since it causes many kinds of health problems [1–3]. Although there are methods to remove chromium such as adsorption [4–6], precipitation [7], ion exchange [8–10], membrane filtration [11–13], their practical application is still limited because of the high operating cost, complicated procedures and sludge formation which again brings about new environmental problems.

Iron oxides nanoparticles (including magnetite and maghemite) are considered to be excellent sorbents for heavy metal ions such as chromium [14,15], arsenic [16–20], copper [21] and cadmium [22]. However, solution dispersible iron oxides nanoparticles also bear

some disadvantages. It is difficult to collect them since they are so small and a strong external magnetic field may be required. Another problem for most iron oxides particles is the aggregation, which results in the reduction of the specific area and therefore a great decrease in the removal potential. In general, iron particles were immobilized on sand [23], slag [24] and cement [25] for arsenic removal from aqueous systems. Recently, polymeric Fe/Zr pillared montmorillonite [26] and montmorillonite-supported magnetite nanoparticles [27] were synthesized and both of them were found to be effective to adsorb Cr (VI) from aqueous solution, suggesting a promising method for the removal of heavy metal ions. However, those are still small particles and a membrane filtration and/or a centrifuge process are required to collect them. Therefore, it is rational to find other feasible methods to facilitate the heavy metal removal process with those high surface area iron oxide nanoparticles.

Porous stainless steel (PSS) support has often been used to support ceramic membranes due to its high mechanical strength, adaptability for fabricating into different shapes, and good corrosion resistance [28]. If iron oxides nanoparticles are

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synthesized on the surface of PSS to form a metal–iron oxides composite membrane, there will be no need to collect the particles and the removal procedure can be achieved during a simple filtration process. Furthermore, this kind of composite membrane is promising to be facily assembled in the membrane sets of water treatment units [29,30] for heavy metal ion removal.

Different methods such as co-precipitation [31], hydrothermal [32], thermal decomposition [33] and sol–gel [34] have been reported for the synthesis of iron oxides nanoparticles. The very classical method to prepare iron oxides nanoparticles is the co-precipitation of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  salts. The size and morphology of the obtained nanoparticles depend on a series of parameters such as reaction temperature, pH and precursor sources; and thus monodispersed, uniform and narrow size distributional magnetite or maghemite particles have been difficult to achieve [35]. Hydrothermal synthesis is usually conducted in a sealed container because of the high temperatures and high pressures [36]. Thermal decomposition was reported to be a very promising method to obtain highly monodisperse magnetite particles with an excellent size tunable potential [37]. But it has a big disadvantage that the resulting particles are generally dispersible in nonpolar solvents only [36]. Sol–gel synthesis usually refers to the hydrolysis and condensation of metal alkoxides or alkoxide precursors [38]. A subsequent sintering process is often required [39] and the particles will unexpectedly aggregate during the process. However, the sol–gel method is very effective to prepare inorganic membranes because it requires relatively simple process and is suitable for coating films on substrates of various shapes [40,41]. This method has been widely used to prepare the intermediate layer [42] and/or top layers [43] on ceramic [44] and metal substrates [45].

In the present study, iron oxides nanostructures were formed by the sol–gel method on PSS to make an inorganic iron oxides membrane for Cr (VI) removal. The preparation parameters including concentrations of casting solutions, multiple coatings, sintering atmospheres and temperatures as well as heating ramp rates were studied. The Cr (VI) removal potential was also evaluated.

## 2. Materials and methods

### 2.1. Preparation of membranes

All the chemicals were of analytical reagent. Solutions were prepared by distilled water. The sol was prepared by the following steps. First, 0.5 mol/L  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  solution was slowly dripped into water–ethylene glycol solution at  $94^\circ\text{C}$  with a volume ratio of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  solution:water:ethylene glycol = 20:50:1 to form a clear brown sol. After the sol was cooled to room temperature, concentrated ammonia was slowly added to adjust the pH value to 2. The sol was then aged for 24 h at room temperature. Casting solutions were prepared by adding 10.5 vol.% N,N-dimethylformamide, 10.5 vol.% glycerol and 26.3 vol.% polyvinyl alcohol (PVA) 1750 solution (concentration of 10 wt.%) into the resultant sol under vigorous stirring. Then a 10-min ultrasonic treatment was employed to make the mixture homogeneous. The concentrations of the casting solutions were calculated by the quantity of Fe in the systems.

Two different shapes of commercial 316L PSS supports with an average pore size of  $\sim 1 \mu\text{m}$  (Shanghai Yiming Filtration Technology Co. Ltd.) were used in the study. One type was small PSS pieces of  $5 \text{ mm} \times 5 \text{ mm}$ , which were cut from a PSS tube. Another type was PSS tubes of 300 mm long, with an inner diameter of 8 mm, and an outer diameter of 10 mm. They were cleaned by dry ethanol and then methyl ketone using an ultrasonic cleaner, and were finally dried at  $300^\circ\text{C}$  for 6 h. The small pieces were used to investigate the impact of fabrication parameters including concentrations of casting solutions, multiple coatings, sintering atmospheres,

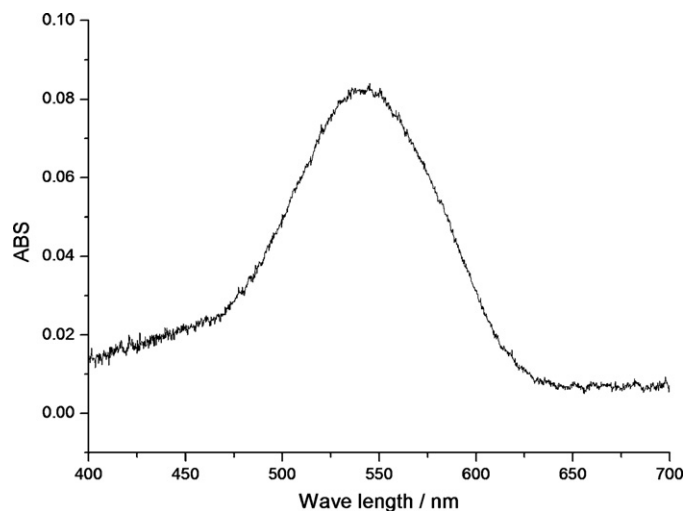


Fig. 1. Light absorption of Cr (VI) – 1,5-diphenylcarbohydrazide.

calcination temperatures and heating ramp rates; the long tubular pieces were used to test the Cr (VI) removal performance. Films on the two types of PSS supports were prepared by dip-coating the supports into casting solutions for 30 s, with a withdrawal rate of 0.5 mm/s. Film sintering was conducted in a multi-segment programmable furnace (SK 2-4-12, Shanghai Shi Yan Electric Furnace Co. Ltd.) in various sintering atmospheres (air and/or nitrogen) at different temperatures (e.g.  $650$ ,  $750$  and  $850^\circ\text{C}$ ) and heating ramp rates (e.g. 1, 5 and  $10^\circ\text{C}/\text{min}$ ).

### 2.2. Membrane characterization

Surface and cross section morphologies of the membranes supported on PSS were characterized by scanning electron microscopy (SEM, JSM-6360) to observe the surface microstructures and the thicknesses of the membranes. The surface SEM samples were used directly with the small pieces and the cross section samples were taken from the small pieces by using cutting pliers. The observation was carried out under an operating voltage of 20 kV and a spot size of 25. X-ray diffraction (XRD) measurements were carried out on a Rigaku D/max 2550 V instrument operating at a voltage of 40 kV and a current of 40 mA with Cu K $\alpha$  radiation in the range of  $20$ – $80^\circ$ . The Cr (VI) removal test was conducted by using a hollow fiber ultrafiltration experimental set (Changzhou Energy Engineering Co. Ltd.). The dead-end membrane module was assembled with the as-prepared tubular membranes which were sealed in a plastic tube. The initial concentration of Cr (VI) was 2 mg/L prepared by dissolving  $\text{K}_2\text{Cr}_2\text{O}_7$  in distilled water. The pH value of the solutions was adjusted to  $\sim 4$  using  $\text{HNO}_3$ . 500 mL of the Cr (VI) test solution was filtered through the dead-end membrane multiple cycles until the Cr (VI) concentration did not change. The flow rate of the Cr (VI) test solution was 8 L/h with a transmembrane pressure of 0.12 MPa. The concentration of each filtered Cr (VI) solution was measured by spectrophotometry (mini UV-1240, SHIMADZU) using 1,5-diphenylcarbohydrazide at a wavelength of 540 nm. The wavelength of 540 nm was selected by scanning a sample containing 8 mg/L of Cr (VI) as shown in Fig. 1 (UV-2550 SHIMADZU).

## 3. Results and discussion

### 3.1. Fabrication of membranes

Fired in air only, continuous membranes with pillar and cubic grains were obtained (Fig. 2a). However, the PSS was somewhat oxidized, which could result in a weakening of the mechanical

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