



# CHROMIUM(VI) REMOVAL BY MODIFIED PVP-COATED SILICA GEL

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## ABSTRACT

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This research involved the synthesizing of a reactive polymer, long alkyl quaternized poly(4-vinylpyridine) (PVP), and coating it on the surface of silica gel to produce a granular sorbent to remove Cr(VI) from water. Batch experiments were conducted to determine the kinetics, sorption isotherm, pH effects, and influence of other anions on the chromium adsorption onto the coated silica gel. The research demonstrated that the synthesized PVP-coated silica gel (referred to as coated gel) could successfully remove chromium(VI) from solution. The adsorption of Cr(VI) by the coated gel was strongly influenced by the pH. The maximum sorption occurred at about pH 4.5-5.5 under the test conditions. The removal efficiency was 100% when the initial Cr(VI) concentration was 2.5 mg/L with 2.5 g/L of coated gel at pH 5.0. The concentrations of Cr(VI) had a pronounced effect on the rate of sorption. Compared to ion exchange, the sorption kinetics of Cr(VI) were fast (about 5h). The equilibrium sorption data fitted the Langmuir isotherm model. Chromium adsorbed on the coated gel was easily recovered under certain conditions.

**Key words:** *chromium(VI), removal, recovery, coated gel, sorption, desorption*

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## 1.0 INTRODUCTION

Chromium compounds are widely used by modern industries, resulting in large quantities of this element being discharged into the environment. Some of the main uses for chromium compounds are as follows: (1) plastic coating of surfaces for water and oil resistance, (2) electroplating of metal for corrosion resistance, (3) leather tanning and finishing, and (4) in pigments and for wood preservative. Until a few years ago, it also was the favored corrosion control agent in cooling towers whose water blowdown (waste) was dumped into rivers, pits, lakes, and oceans (Norvelle, 1992). In addition, during the 1950's, chromates were used as a highway de-icing agent in the United States. Chromium occurs in wastewaters resulting from these operations in both trivalent [Cr(III)] and hexavalent [Cr(VI)] forms. The hexavalent form is more hazardous to animals than the trivalent form.

A wide range of technologies is available for the removal of hexavalent chromium from wastewaters, some of which are well-established methods that have been in practice for decades such as precipitation, coprecipitation (Patterson and Passino, 1987), and concentration (U.S. EPA, 1980). These processes simply remove chromium from wastewaters by reduction (Shen and Wang, 1995), coagulation, and filtration. Although these technologies are quite satisfactory in terms of purging chromium and other heavy metals from water, they produce solid residues (sludge) containing toxic compounds whose final disposal is generally by landfilling with related high costs and still a possibility of groundwater contamination. From the environmental point of view, removing pollutants from liquid wastewater does not solve the problem but transfers it from one phase (usually liquid) to

another phase (usually solid). Chromium (III) toxicity to mammals and aquatic organisms appears to be lower compared to Cr(VI), due to generally low solubility of its compounds (Ciavatta, et al. 1992). However, the possibility that the presence of organic ligands and/or acidic conditions in the environment increases Cr(III) mobility, and also  $\text{MnO}_2$ , present in soil, could oxidize Cr(III) to the more toxic and mobile Cr(VI) forms (Heary and Ray, 1987), cannot be excluded. Accordingly, the practice of landfilling and land application of chromium-contaminating sludge should be discouraged. Thus, these methods have the following problems: secure landfill costs are high; land application and landfill may contaminate the groundwater.

Emphasis in recent years has been on methods for recovery and reuse of metals rather than disposal. These include activated carbon adsorption (Ouki and Neufeld, 1997), liquid-liquid extraction (Clevenger, 1983), liquid membrane separation (Fraser and Pritzker, 1994), ion exchange, biosorption (Brower, 1997; Petruzzelli, 1995), and chelating resins and reactive polymer methods (Chen, 1995; Tiravanti, 1996).

Chen (1995) assessed 190 ligands for their ability in extraction and recovery of target metals, including cadmium, copper, lead, mercury, nickel, and zinc. Chelator performance was evaluated based on equilibrium calculations with an emphasis on the potential of recovering both the metals and the chelating agents. Macauley and Hong (1995) used PDA as a lead-complexing agent, which was better than EDTA in releasing the extracted lead.

Tiravanti et al. (1996) used natural and synthetic polymers for selective metal removal, recovery, and reuse. They used a weak cation (carboxylic) ion exchange resin and allowed for recovery and reuse of 90% chromium from other interfering metals such as Fe and Al. However, this resin was only used for removal of Cr(III). In order to reuse  $\text{CrO}_4^-$ , the oxidant ( $\text{H}_2\text{O}_2$ ) and acidic solution had to be included in the regeneration steps, which increased the cost of the process.

Santiago (1995) used tailored zeolites, which were modified by replacing naturally occurring inorganic cations with long alkyl quaternary ammonium ions for removal of Cr(VI). The study showed that the efficiency of Cr(VI) removal depended on the properties of the zeolite, including surface area and external cation exchange capacity (ECEC); the physical properties; and the dosage of the tailoring agent. Efficiency of removal also depended on the solution properties, such as pH and ionic strength. The disadvantages of this method were the inability to regenerate and recover the Cr(VI) and the reuse of the tailored zeolites.

Chanda (1993) reported a new reactive polymer granular sorbent for uranyl sulfate ( $\text{UO}_2\text{SO}_4$ ) recovery, which was developed by gel coating a weak-base resin poly(4-vinylpyridine) (PVP) as a lightly cross-linked thin layer on high-surface-area silica gel. The gel coating of the resin afforded nearly 80% attainment of its theoretical capacity and provided fast sorption kinetics and nearly instantaneous stripping as compared to conventional weak- and strong-base resins at a relatively high pH (>4).

The polymer developed by Chanda (1993) was used in this research after modification to promote Cr(VI) sorption. The pyridine unit of the polymer was quaternized by using 1-bromohexadecane as a quaternization agent.

In order to solve the two problems which existed in the ion exchange process for metal ion removal, i.e., (1) low sorption capacity at equilibrium conditions and (2) slow sorption rate, which is related to degrees of inaccessibility of sorption sites, the sorbent was prepared as a thin gel layer on a high-surface-area substrate for improving the sorption process and reducing these two problems.

The reactive polymer-coated gel had the following advantages: (1) fast kinetics, (2) high selectivity for Cr(VI), (3) large capacity per unit weight, (4) high recovery efficiency, (5) low waste production, and (6) easy recovery of Cr(VI) for reuse. The developed process should have commercial applications.

## **2.0 MATERIALS AND EXPERIMENTAL PROCEDURES**

### ***2.1 Materials and Regents***

Chromium solution of 1000ppm was obtained from Fisher Scientific Co., which was a reference standard solution. The standard Cr(VI) solution was diluted to the desired concentration using deionized water (DW) when needed. DW was obtained from the College of Engineering at University of Missouri-Columbia (MU) centralized purified water system.

All glassware and plasticware were washed with soap and water, followed by a tap rinse, acid rinse with 1N HCl, and three final rinses with deionized water.

### ***2.2 Preparation of Reactive Polymer***

The polymer—poly(4-vinylpyridine) (PVP) used was prepared by bulk polymerization of 4-vinylpyridine using cumene hydroperoxide as an initiator [0.5% (w/v)] at 55°C. 100 g silica gel was soaked in 250 ml of 2% (w/v)  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  solution and evaporated to dryness in water bath with continuous mixing (I). PVP (12g) was dissolved in 1000mL of chloroform (II). Reagent (I) was added to reagent (II), agitated with a paddle stirrer for 6h. Chloroform was decanted, and the polymer impregnated gel (III) was washed several times with methanol. The gel (III) was dispersed in 300 ml of methanol to which the cross-linking reagent 1,4-dibromobutane was added (in steps) to the extent of 50% the theoretical amount required for cross-linking the pyridine. The mixture was vigorously stirred at 65°C for 96 hrs in a slow current of nitrogen. In order to synthesize the long alkyl chain quaternary ammonium compound, 1-bromohexadecane was used as a quaternization agent. The above mixture was washed successively with 2 M  $\text{NH}_4\text{OH}$  and 2 M NaCl, which gave the lightly cross-linked polymer (IV). The mixture (IV) was dispersed in 250ml methanol to which 1-bromohexadecane was added to the extent of 200% in excess of the theoretical amount required for reaction with all the residual pyridine units. The mixture was agitated at 68°C for 72 hrs in a slow current of nitrogen. The product was filtered and washed with methanol, 2M NaCl solution, 2M

HCl, and water to obtain the final polymer (modified PVP) (Chanda and Rempel, 1994). Figure 1 is the flow chart of the preparation processes.

Figure 2 shows the possible structures of the reactive polymer: (a) the structure of PVP formed in the polymerization process, (b) protonated PVP under acid conditions, and (c) 1,4-dibromobutane cross-linking or 1-bromohexadecane quaternized PVP.

### 2.3 Chromium Sorption Experiments

The sorption studies were carried out at room temperature (25°C). The pH of the solution containing the desired quantity of chromium(VI) was adjusted by adding 0.1 M HCl or 0.1 M NaOH. A desired quantity of the long alkyl quaternized poly(4-vinylpyridine) (modified PVP)-coated gel was placed in a separate test tube with the pH-adjusted Cr(VI) solution. One sample of the same concentration solution without the sorbent was also prepared and treated under the same conditions as the tube containing sorbent (control). This control was used as a reference to establish the initial concentration for the tube containing the sorbent. The test tubes were capped and placed on a Wrist-Action Shaker (Model 75, manufactured by Burrell Corporation) for 20 hrs for the equilibrium studies, or on a Thermolyne Maxi-Mix mixer (manufactured by Barnstead Thermolyne Corporation) for the non-equilibrium studies. The test tubes were then removed and the solution filtered using a filter paper (Whatman 5, pore size 2.5 mm). The concentration of chromium(VI) in aqueous phase was determined by a Perkin Elmer Atomic Absorption Spectrophotometer Model 2380. The operational parameters of the atomic absorption spectrophotometer are summarized in Table 1. The amount of chromium adsorbed was determined by subtracting the final concentration from the initial concentrations. If the chromium concentration in the solution was smaller than 5 mg/L, the solution was measured directly using Atomic Adsorption Spectrophotometer; if the concentration was greater than 5 mg/L, the solution was diluted with deionized water to 0.5-4.0 mg/L before measurement by the spectrophotometer.

In order to evaluate the adsorption of chromium onto the reactive polymer coating gel, Freundlich and Langmuir isotherms were used as the adsorption models. The Freundlich adsorption isotherm consisted of a curve plotted with equilibrium concentration of the solute in solution on the “x” axis and the amount adsorbed per unit weight of adsorbent on the “y” axis. Thus, any point on the line gives the adsorption capacity or loading at a particular equilibrium concentration in solution. The liquid-phase concentration at equilibrium was analytically determined. The solid-phase concentration was determined from a mass balance on the batch reactor. The equations are as follows (Weber, 1972):

$$q = (C_0 - C_e) \frac{V}{m} \tag{Eqn. 2-1}$$

$$q = \frac{x}{m} = kC_e^{\frac{1}{n}} \tag{Eqn. 2-2}$$