



CHAPTER I
INTRODUCTION

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Nowadays disposal of chromium-containing wastewater has become a serious environmental problem to the industries. Chromium compounds are widely used in the manufacture of ceramics, catalysts, pigments, wood preservatives and fungicides, in metal finishing, in corrosion control, in tanning industry, in magnetic tapes and in printing and dyeing of textiles (Westbrook, 1993).

Two stable oxidation states of chromium occur in natural environments are chromium (VI) and chromium (III). Hexavalent chromium is more toxic than trivalent chromium (Westbrook, 1993). Occupational exposure to chromium (VI) is of concern because it is non-biodegradable and highly toxic compound; moreover, it has mutagenic and carcinogenic effect. Effects on the body include skin ulceration, inflammation of air passages, allergic reactions, and lung cancer.

Various methods have been used to remove chromium from industrial waste water. The traditional techniques for removal of chromium ion from aqueous effluents, which are lime precipitation or process of reduction, are incapable of reducing concentration to the levels required by law. Drinking water standards have been set at 0.1 mg/L total chromium (Page and Loar, 1993). Although these conventional processes generate the large amount of hydroxide solid at the end of the process, they have been widely used in industries. The other methods including electrochemical precipitation (Kongsricharoen and Polprasert, 1995, 1996), ion exchange (Zhao *et al.*, 1998) and activated carbon adsorption (Lalvani *et al.*, 1998) are prohibitively expensive. Moreover, these processes are still in developing stages.

The use of membrane separation process in treating wastewater containing metal ions is today an attractive and suitable technique because the separation can be carried out at room temperature, the modular membrane can be easily adjusted to the wastewater flows; and various industrial membranes are now available. In order to retain chromium ions, reverse osmosis is used. Reverse osmosis is a membrane process, which applies pressure forces water to pass through a semi-permeable membrane, which prevents the passage of dissolved and suspended constituents (Tucker *et al.*, 1992). But the usual permeate fluxes of reverse osmosis membranes are limited and require high transmembrane pressure (200-800 psi), which makes the

process expensive. In addition, the reverse osmosis process is often affected by fouling, scaling, and chemical deterioration of the membrane

Ultrafiltration is an attractive industrial separation technique for removing molecules from wastewater; however, traditional ultrafiltration is not effective in removing solutes having molecular weight less than 500 Daltons (Christian *et al.*, 1995). A new class of ultrafiltration techniques developed is called colloid-enhanced ultrafiltration (CEUF) (Christian *et al.*, 1990, 1995). These technologies all involve adding water-soluble colloids to aqueous stream and subsequently using ultrafiltration to remove target ions and molecules that could not be effectively removed by ultrafiltration. The techniques that have been investigated up to the present include micellar-enhanced ultrafiltration (MEUF) (Scamehorn *et al.*, 1986, 1994; Dunn *et al.*, 1985, 1987; Bhat *et al.*, 1987; Smith *et al.*, 1987; Christian *et al.*, 1988; Choi *et al.*, 1998; Gzara and Dhahbi, 2001), polyelectrolyte-enhanced ultrafiltration (PEUF) (Sasaki *et al.*, 1989; Novikov *et al.*, 1989; Tucker *et al.*, 1992a, 1992b; Mundker and Watters, 1993; Volchek *et al.*, 1993; Zhou *et al.*, 1994; Tabatabai *et al.*, 1995a, 1995b; Geckeler and Volchek, 1996; Juang and Chen, 1996; Sriratana *et al.*, 1996; Uludag *et al.*, 1997; Muslehddinoglu *et al.*, 1998; Tangvijitsri *et al.*, 2002), polyelectrolyte-surfactant complexes in CEUF (Guo *et al.*, 1997), ligand-modified micellar-enhanced ultrafiltration (LM-MEUF) (Klepac *et al.*, 1991; Fillipi *et al.*, 1997, 1998), ligand-modified polyelectrolyte-enhanced ultrafiltration (LM-PEUF) (Tuncay *et al.*, 1994a, 1994b) and ion-expulsion ultrafiltration (IEUF) (Christian *et al.*, 1989; Krehbiel *et al.*, 1992).

In PEUF, a water-soluble polyelectrolyte, of charge opposite to that of the soluble target ion, is added to the polluted water. The target ion binds or adsorbs onto the polyelectrolyte. The solution is then treated by ultrafiltration with membrane pore size small enough to reject the polyelectrolyte. The purified water (permeate) may be released to the environment. If the permeate is not sufficiently low, the process can be staged to achieve any desired degree of purity.

Ions, which have been studied in PEUF, include divalent cations such as copper (Sasaki *et al.*, 1989; Mundker and Watters, 1993; Volchek *et al.*, 1993; Geckeler and Volchek, 1996; Juang and Chen, 1996), nickel (Volchek *et al.*, 1993; Geckeler and Volchek, 1996), cadmium (Volchek *et al.*, 1993; Geckeler and

Volchek, 1996; Müslehddinoglu *et al.*, 1998), cobalt (Volchek *et al.*, 1993; Geckeler and Volchek, 1996), zinc (Volchek *et al.*, 1993; Geckeler and Volchek, 1996), mercury (Geckeler and Volchek, 1996; Uludag *et al.*, 1997; Müslehddinoglu *et al.*, 1998), calcium (Tabatabai *et al.*, 1995; Geckeler and Volchek, 1996; Müslehddinoglu *et al.*, 1998), magnesium (Tabatabai *et al.*, 1995; Geckeler and Volchek, 1996) (with an anionic polyelectrolyte), divalent anions such as chromate (Tucker *et al.*, 1992a, 1992b; Sriratana *et al.*, 1996; Tangvijitsri *et al.*, 2002), sulfate (Tangvijitsri *et al.*, 2002), monovalent anion such as nitrate (Tangvijitsri *et al.*, 2002), and multivalent anions such as arsenic or arsenate (Shkinev *et al.*, 1987; Geckeler and Volchek, 1996; Legault *et al.*, 1993), actinides (Novikov *et al.*, 1989) and selenite or selenate (Geckeler and Volchek, 1996) (with a cationic polyelectrolyte)

In the purification of water containing chromate, the cationic polyelectrolyte poly(diallyldimethylammonium chloride) or QUAT is used in removing chromate over a wide range of chromate and QUAT concentrations, as well as different concentrations of added NaCl. In the absence of other added electrolytes, chromate rejections of up to 99.8% were observed. The presence of added NaCl reduces the chromate rejection substantially. The results also gave high gel concentration and high rejection (Sriratana *et al.*, 1996; Tangvijitsri *et al.*, 2002).

An efficient and economic process would consist of a further step to separate the polymer/chromate mixture to provide a compact chromate waste for disposal and a polyelectrolyte-rich stream, which could be returned to the process. The most direct route toward freeing the chromate from the polyelectrolyte and producing a compact chromate waste appears to be a precipitation step. The precipitant for chromate, which might be least environmentally harmful in low concentration, appears to be barium chloride. The chloride ion will reconstitute the polyelectrolyte with its chloride counterion and barium chromate may be separated as a solid waste, which settles out, so that inexpensive gravity settling is feasible. The integrated PEUF and regeneration processes were demonstrated in a field test to treat groundwater, which contained chromate from electroplating waste at the Elizabeth City Coast Guard Base in North Carolina, however, the overnight settling in a quiescent was used for the precipitating step (Tucker *et al.*, 1992a, 1992b)

For industrial operation, a continuous, steady state separation using high flow rate is generally less expensive to operate than a batch process. So this research work was focused on the feasibility of the continuous polyelectrolyte recovery process using a continuous crystallizer. In addition, the studies of the equilibrium precipitation of barium chromate in a laboratory scale, the polymer recovery in a batch crystallizer, and the effect of polyelectrolyte on barium chromate dispersion stability were parallely carried out in order to comprehend phenomena occurred in the continuous polyelectrolyte regeneration process.