CHAPTER VI

QUATERNIZATION OF POLY(4-VINYL PYRIDINE)
SONOCHEMICALLY WITH IODOETHANE AND STUDY OF ITS
Cr(VI) SORPTION ABILITY

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VI.1 INTRODUCTION

Cationic polyelectrolytes, in general, have many potential applications in sludge dewatering [1], design of new membrane [2], phase transfer catalysis [3], ion exchange separation [4] and stabilization of dispersions [5] (as lubricating agents, emulsifier, flocculating agents, etc.). Most outstanding examples of cationic polyelectrolyte are quaternary ammonium polymers. Diallyl dimethyl ammonium chloride [6] (DDAC), methacryloyloxy ethyl trimethyl ammonium chloride [7] (METAC) and vinyl benzyl trimethyl ammonium chloride [8] (VBTAC) are some commercially available quaternary ammonium monomers which lead to quaternary ammonium polymers. Preparation of vinyl pyridinium monomers is difficult due to their spontaneous polymerization yielding pyridinium moieties in the main chain [9]. Many studies have been carried out involving the quaternization of poly(4-vinyl pyridine) [10-11] and related compounds with alkyl and aryl halides. A recently available macro porous resin, Reillex™ HPQ [12], which is derived from poly(4-vinyl pyridine) by quaternization to the extent of about 70 % and is reported to offer much higher resistance to oxidation than conventional strong base polystyrene anion exchanger resins [12], Amberlite IRA-400. Typically, 65-70 % quaternization is most common with alkyl halides. Quantitative quaternization [10] of poly(4-vinyl pyridine) and the preparation of quaternized poly(4-vinyl pyridine) nanoparticles [13] are important goal to be achieved. Moreover, most of the quaternization reactions are carried out in polar organic solvents [10-14] such as tetrahydrofuran, dimethyl formamide, methanol, etc. Quaternized and cross-linked copolymers from vinyl pyridine and di-halo organic compound are formed spontaneously at ambient temperature by just mixing the two monomers in bulk, in solution or on suspension. The main disadvantage here is the uncontrolled molecular weight of the resulted polymers.

It is noteworthy to mention here that in spite of very high sorption selectivity of Cr(VI) anions on commercial organic anion-exchange resin [12], Amberlite IRA-400, recovery of chromate from cooling tower blow down is not yet commercially popular. The slow oxidation of the resins by Cr(VI) and consequent loss of resin capacity prevented more frequent application of the ion exchange process [15]. In this context, it may be noted that quaternized poly(vinyl pyridine) [16-17] has been shown to exhibit greater stability to
chemical attack and radiolysis degradation than polystyrene. The greater stability of quaternized poly(vinyl pyridine) to chemical oxidation is exhibited due to the electron deficiency of its ring system.

The remarkable oxidation resistance of the quaternized poly(vinyl pyridine) and its very high selectivity of chromate interested us to search green technique for quantitative quaternization of poly(4-vinyl pyridine) and to develop a suitable method for selective sorption and desorption of Cr(VI) from aqueous solutions of wide pH range (from acidic to basic) using the quaternized polymer. The measured sorption and desorption properties are compared with those of a commercially available resin Reillex™ HPQ and IRA-400.

VI.2 QUATERNIZATION OF POLY(4-VINYL)PYRIDINE SONOCHEMICALLY

The quaternization was performed with the help of ultrasound using a sonicator (Branson 1510) in aqueous medium in the presence of quaternizing agent. P4VP (colorless, 2.62 g) was soaked with 1.35 g iodoethane in 20 mL distilled water, and subjected to sonication at room temperature for just an hour. The reaction mixture was then centrifuged to obtain a solid (yellow) which was washed several times with water and alcohol, filtered and dried under vacuum at room temperature to a constant weight (3.93 g). The size, surface area and anion exchange capacity of the quaternized product was found to be 0.25-0.50 mm, 9.2 m².g⁻¹, 4.5 meq.g⁻¹ respectively (Table 6.2.1)

Table 6.2.1. Characteristics of the synthesized polymer:

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Structural unit</th>
<th>Particle size (mm)</th>
<th>Surface area (m².g⁻¹)</th>
<th>Anion exchange capacity (meq.g⁻¹)</th>
<th>Water content % (w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P4VP</td>
<td>-CH₂-CH⁻</td>
<td>0.20-0.40</td>
<td>8.5</td>
<td>2.1</td>
<td>44 %</td>
</tr>
<tr>
<td></td>
<td><img src="image" alt="Structure" /></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Q4VP</td>
<td>-CH₂-CH⁺</td>
<td>0.25-0.50</td>
<td>9.2</td>
<td>4.5</td>
<td>57 %</td>
</tr>
<tr>
<td></td>
<td><img src="image" alt="Structure" /></td>
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</tr>
</tbody>
</table>

These parameters are much improved than commercially available widely used anion exchanger Amberlite-400 and comparable to that of Reillex™ HPQ [12].
VI.3 IODIDE ANALYSIS

The quaternized poly(4-vinyl pyridine), (QP4VP) was characterized chemically (iodide analysis). The quaternization yield was followed by analysis of the iodide of the final product. Thus 0.3 g of the quaternized beads was boiled in 20 mL of 20 % KOH solution for 2 h. The mixture was filtered and washed with 30 mL distilled water. The filtrate and washing were combined and neutralized with 3M HNO₃. The solution was transferred in a 100 mL volumetric flask. The analysis of the iodide was performed iodometrically [18]. The iodide content of the product indicates quantitative quaternization. The product contains an iodide ion per nitrogen centre approximately.

VI.4 CHARACTERIZATION OF SOLID PHASE

The characterization of solid phase (QP4VP) was performed both in presence and absence of Cr(VI). The chromate sorption was determined with Cr(VI) solution (96.47 ppm) at pH 5.6 with an agitation time 60 min. After this period, the solid phase was dried and analyzed by SEM. FTIR, TGA, and DTA. The FTIR spectrum was recorded using KBr pellets by Shimadzu-8400S spectrometer. TGA and DTA were recorded using a Perkin Elmer TGA/DTA (STA-6000) thermal analyzer in nitrogen atmosphere at a heating rate of 10 oC/min. SEM of the solid phase was conducted using JEOL SEM 6360 apparatus.

The scanning electron micrograph (Fig. 6.4.1) showed the bead shape and gel morphological structures of the prepared polymer.

![Fig. 6.4.1. Scanning electron micrograph of the quaternized polymer, QP4VP](image)
Fig. 6.4.2 shows the FTIR spectra of P4VP (A), QP4VP (B) and QP4VP loaded with Cr(VI) (C) at pH 5.6. The comparison of the spectra of P4VP and QP4VP revealed that a new peak at 1640 cm\(^{-1}\) is appeared in B and the characteristic band at 1600 cm\(^{-1}\) is disappeared from A. The peaks at 1600 and 1640 cm\(^{-1}\) may be assigned to tertiary [3, 13] and quaternary ammonium [3, 13] groups respectively. Thus, the complete shifting of peak from 1600 to 1640 cm\(^{-1}\), may be treated as quantitative quaternization of P4VP. **Fig. 6.4.2.** C shows characteristic signal of Cr-O bond [15] of both CrO\(_4^{2-}\) and Cr\(_2O_7^{2-}\) at 875 cm\(^{-1}\).

![FTIR spectra of P4VP (A), QP4VP (B) and QP4VP loaded with Cr(VI) (C)](image)

The result confirms the retention of Cr(VI) by QP4VP. On the basis of FTIR study a model of interaction between QP4VP and Cr(VI) has been proposed (**Fig. 6.4.3**) [3].

![Model proposed for interaction between QP4VP and Cr(VI) at different pH](image)
Fig. 6.4.4 shows the thermal degradation profile of P4VP (A), QP4VP (B) and Cr(VI) loaded QP4VP (C). The profile reveals that quaternized products (B and C) are less stable than starting material (A) as the decomposition starts around 400 and 500 °C for the former and later case respectively. Besides, it can be observed that P4VP and QP4VP have a total mass loss of 100 %, but the Cr(VI) loaded species shows mass loss of approximately 90 %. The remaining 10 % mass corresponds to the presence of Cr(VI) oxides without decomposition. As can be seen, there is, in all cases, a slight weight loss around 100 °C, which can attributed to the evaporation of water molecules. Moreover, the derivatives of P4VP contain some of residual quaternizing agent ethyl iodide whose boiling point is 70 °C. The loss of residual quaternizing agent is reflected from the degradation pattern between 200-300 °C. In addition, the degradation mechanism of QP4VP is bimodal as compared to that of P4VP which is unimodal.

**VI.5 EFFECT OF SORBATE DOSE ON SORPTION**

Effect of chromium ions (sorbate) present initially in the aqueous solution was studied in order to assess the concentration range of chromium which can be treated by the present material. The extent of sorption ($q_t$) increased with the increase of sorbate dose (5-1000 mg L$^{-1}$) (Fig. 6.5.1) reaching a plateau at about 1000 mg L$^{-1}$, which corresponds to 100 % use
of the ion exchange capacity. The maximum sorption capacity was found to be 120 mg.g$^{-1}$, which may treated as better results compared to the poly(4-vinyl pyridine) quaternized with 2-chloroacetamide [14] (95 mg.g$^{-1}$), benzyl chloride [17] (70 mg.g$^{-1}$), 2-chloroacetone [17] (75 mg.g$^{-1}$), and commercially available anion exchange, Amberlite-400 [12] (108 mg.g$^{-1}$) and Reillex™ HPQ [12] (112 mg.g$^{-1}$).

![Graph](image)

**Fig. 6.5.1.** Variation of sorption capacity with initial metal ion concentration  
(Sorbent dose = 8 g.L$^{-1}$, pH=5.6, Temperature = 30 °C)

### VI.6 EFFECT OF pH ON SORPTION

Sorption of chromium was studied at various pH values to determine the optimum pH range for its removal and the results are presented in **(Fig. 6.6.1)**. The pH was adjusted with the additions of diluted sodium acetate and acetic acid. The sorption of Cr(VI) is fruitful at pH values between 3.0 and 8.0. It is noteworthy to mention here that most of the anion exchange resin functions well between 3.0 and 5.0 (acidic medium) and deactivates in the basic medium. The favorable wide pH range (both acidic and basic) may be explained from the model (**Fig. 6.6.1**). At very low pH (<3), the Cr(VI) remains mainly as non-ionic form (H$_2$CrO$_4$), which accounts for its low sorption. At pH>8, the hydroxyl ion competes with chromate ion resulting low chromium sorption. The rest of the experiment was done at pH 5.6, because pH of effluent of many chrome industry lies in the same order.
Fig. 6.6.1 Variation of sorption capacity with pH

[Sorbent dose = 8 g.L\(^{-1}\), sorbate dose = 47.16mg.L\(^{-1}\), Temperature = 30 °C]

The pH dependent sorption mainly takes place through ion exchange process (Eq\(^n\). 6.6.1). It was supported by the fact that the addition of halide desorbs the chromate ion. Potassium iodide acts as very good stripping agent for the present system.

\[
2 \overset{+}{\equiv} N-O^{-} (S) + \underset{+}{Cr} O_7^{2-} (aq) \rightleftharpoons \overset{+}{\equiv} N-O^{-} (S) + 2 \underset{+}{Cr} O_7^{2-} (S) + 2 X^{-} (aq)
\]

............................... (6.6.1)

VI.7 SORPTION KINETIC

It is a well-established fact that the sorption of ions from aqueous solutions is reversible and follows reversible first order kinetic when a single species is considered on a heterogeneous surface [16]. The progress of the sorption process was monitored at different time intervals (Fig. 6.7.1). The Cr(VI) sorption with respect to time was smooth and continuous leading to saturation after an hour showing monolayer coverage of metal ions on the surface of the resin.
Chapter VI

VI.8 EFFECT OF THE SO$_4^{2-}$ AS COMPETITIVE IONS

Since sulfate and chloride are the predominant anionic species in cooling tower blow-down, the resin must have high sorption selectivity for Cr(VI) over these competing anions. To measure the selectivity, equilibrium chromate sorption was measured in the presence of 200-fold molar excess of SO$_4^{2-}$ and 400-fold molar excess of Cl$^-$ at different levels of pH of the aqueous medium (Fig. 6.8.1). The selectivity ($S$) defined [12] as:

\[
S = \frac{\text{Cr(VI) sorption in presence of SO}_4^{2-}/\text{Cl}^-}{\text{Cr(VI) sorption in absence of SO}_4^{2-}/\text{Cl}^-}.
\]

\[\text{Eqn. 6.8.1}\]

The selectivity value was found to be greater than 0.5 over the pH range 3 to 8, which suggested the preference of chromate over both sulfate and chloride. It is well-known that the selectivity order for the common anions of the commercially available styrene anion exchanger is: SO$_4^{2-}$> I$^-$> CrO$_4^{2-}$ > Br$^-$> Cl$^-$. In our case, the synthesized resin showed a reversal selectivity namely CrO$_4^{2-}$ > SO$_4^{2-}$ > Cl$^-$. It is reported [12] that at high concentration of bisulfate (pK$_2$ = 2.1) and chloride, HCrO$_4^-$ may form mononuclear complexes (Eqn. 6.8.2 & 6.8.3) at acidic medium.
HSO₄⁻ + HCrO₄⁻ = CrSO₄²⁻ + H₂O; \quad K = 4.1 \quad \ldots (6.8.2)

HCrO₄⁻ + H⁺ + Cl⁻ = CrO₃Cl⁻ + H₂O; \quad K = 17.1 \quad \ldots (6.8.3)

Mononuclear Cr(VI) complexes (CrSO₄²⁻ and CrO₃Cl⁻) are likely to be present in the exchanger phase at fairly high HSO₄⁻ and Cl⁻ level at the acidic medium. Thus the synthesized polymer had little preference below pH 3. Strong competition for exchange sites by SO₄²⁻, Cl⁻ and OH⁻ at alkaline pH where the aforesaid mononuclear complex might not form and was possibly responsible for the sharp fall in Cr(VI) sorption at pH>8.

![Fig. 6.8.1. Preference for Cr(VI) sorption as a function of pH in the presence of sulfate and chloride ion](image)

[Cr(VI) = 47.16 mg.L⁻¹, Sorbent dose = 8 g.L⁻¹, Temperature = 30 °C, Time = 1 h]

### VI.9 SORPTION ISOTHERM

The effect of temperature on the sorption has been studied by performing sorption experiments in the temperature range of 5-55 °C. The result suggests that the equilibrium reaches rapidly with the increasing temperature. For the equilibrium sorption isotherm study in a two-component system consisting of sorbent and solution, a plot of the solute concentration in the solid phase, Q (mg.g⁻¹) as a function of the solute concentration in the solution, Cₑ (mg.L⁻¹) at equilibrium was drawn (Fig. 6.9.1). In a solid liquid system, the
sorption resulted in the removal of solute from the solution onto solid surface until the remaining solute in the solution is in dynamic equilibrium with solute on the solid phase.

The Langmuir equation [7] was basically derived for the sorption of gases on the solid surface. Nevertheless, it has been extended to include the sorption of solute at solid-liquid interface [15, 17]. The Langmuir isotherm is valid for monolayer sorption onto the surface containing a finite number of identical sites and the standard mathematical representation is:

\[ \frac{C_e}{q_e} = \frac{1}{Q_m \times b} + \frac{C_e}{Q_m} \]  \hspace{1cm} (6.9.1)

Where \( C_e \) is the equilibrium concentration of chromium in the solution (mg.L\(^{-1}\)); \( q_e \), the amount of the retained chromium (mg.g\(^{-1}\)); \( Q_m \) is the maximum sorption capacity (mg.g\(^{-1}\)) and \( b \) is the Langmuir constant related to the affinity of binding sites. The essential feature of Langmuir sorption can be expressed by means of \( R_L \), a dimensionless constant referred to as a separation factor or equilibrium parameter for the prediction if the sorption system is favorable or not. \( R_L \) can be calculated using the equation:

\[ R_L = \frac{1}{1 + b \cdot C_0} \]  \hspace{1cm} (6.9.2)

\( C_0 \) is the initial concentration of the chromate solution (mg.L\(^{-1}\))

The Freundlich isotherm model [7] assumes that the sorption of metal ions occurs on a heterogeneous sorbent surface. Freundlich equation is expressed as:

\[ \log (Q/m) = \log K_F + \frac{1}{n} \log C_e \]  \hspace{1cm} (6.9.3)

\( Q \) is the amount of retained chromium (mg.g\(^{-1}\)); \( m \) is the amount of the resin (g.L\(^{-1}\)); \( C_e \) is the concentration at equilibrium (mg.L\(^{-1}\)); \( K_F \) and \( n \) are Freundlich constants.

The Langmuir and Freundlich sorption parameters were determined by plotting the experimental data based on Eq\(^n\). 6.9.1 and 6.9.3 respectively. The parameters were determined and their corresponding correlation coefficient (\( R^2 \)) was listed in Table 6.9.1. The parameters clearly suggests for favourable sorption of chromate ions. The \( R_L \) values obtained in the present case are less than 1 and very close to 0 and therefore, they also indicate a favourable sorption.


**Fig. 6.9.1.** Effect of equilibrium sorbate dose on chromate ion adsorption

**Table 6.9.1.** Values of Langmuir and Freundlich constants for the sorption of Cr(VI)

<table>
<thead>
<tr>
<th>$T(°K)$</th>
<th><strong>Langmuir Constants</strong></th>
<th><strong>Freundlich Constants</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R_L$</td>
<td>$Q_m$</td>
</tr>
<tr>
<td>278</td>
<td>5.031x10$^{-3}$</td>
<td>12.74</td>
</tr>
<tr>
<td>303</td>
<td>2.04x10$^{-3}$</td>
<td>8.39</td>
</tr>
<tr>
<td>328</td>
<td>1.34x10$^{-3}$</td>
<td>7.41</td>
</tr>
</tbody>
</table>

**VI.10 DESORPTION STUDY**

QP4VP (0.2 g) was taken in a 100 ml beaker with 25 mL of Cr(VI) solution (96.47 mh.L$^{-1}$) at pH 5.6 and kept for 1 h at room temperature. The absorbed Cr(VI) was then subjected to various stripping agents such as Na$_2$CO$_3$, NaOH, NaCl and KI to desorbs chromate. KI (>1M) was found to be the most fruitful stripping agents. It desorbed to the extent of 88.88 %. Other agents gave fairly lesser extent of desorption.
VI.11 CONCLUSION

- Quaternization of poly(4-vinyl pyridine) with iodoethane has been achieved in aqueous medium sonochemically. The novelty of the quaternization method is quantitative as well as green.
- The synthesized resin may be used to remove and recover Cr(VI) from the aqueous solution through batch method within the pH range 3-8 at ambient temperature.
- Competitive ions like \( \text{SO}_4^{2-} \) and \( \text{Cl}^- \) do not hamper the Cr(VI) sorption up to pH 8.
- The sorption and de-sorption of Cr(VI) mainly take place through ion exchange process. Sorption takes place very quickly.
- Isothermal sorption experimental data obey both Langmuir and Freundlich model.
- Potassium Iodide behaves as a fruitful stripping agent.
VI.12 REFERENCES