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Use of poly(4-vinylpyridine) based crosslinked poly(ionic liquid) as anion exchangers for the extraction of Ni^{2+} metal ions

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Abstract: *The quaternization of nitrogen containing polymers with alkylating agents raise their spectrum in many applications and the preparation of poly (ionic liquids) [PILs] is one of the great developments. PILs are very attractive materials, and have mainly used as anion exchangers. As the PILs are made of ions, therefore, these can be used as packing material in ion-exchange chromatography for the extraction of different metal ions. PILs act as anion exchangers as in these positively charged beads associate with, and therefore, exchange with negatively charged counter ions and hence metal ions be extracted as their anions. In present study poly(4-vinylpyridine) based crosslinked poly(ionic liquid) has been used as anion-exchangers for the extraction of Ni^{2+} metal ions from the aqueous solution. The extraction of Ni^{2+} was done by way of changing it to $NiCl_4^{2-}$. Nickel is a strong chloride ion acceptor and mainly exists as $NiCl_4^{2-}$ anion in the NaCl solution; therefore, it can be changed to anion by adding the NaCl solution and after it is changed to anion, it can be extracted from the solution by using anion exchangers. The extraction of Ni^{2+} metal ion was studied as a function of time, different NaCl concentration and temperature.*

Key Words: *Nickel metal ions extraction, poly(4-vinylpyridine), anion-exchanger, poly (ionic liquids)*

1. INTRODUCTION:

The quaternization of nitrogen containing polymers with alkylating agents raise their spectrum in many applications and the preparation of poly (ionic liquids) [PILs] is one of the great developments. PILs have a large number of potential activities, and are mainly used as surfactants (1,2), antimicrobial agents (3–6), CO_2 adsorbents (7,8) and anion exchangers in extraction of different metal ions (9-11). As the PILs are made of ions, therefore, these can be used as packing material in ion-exchange chromatography for the separation/purification of products such as nutritional proteins and enzymes (12).

PILs act as anion exchangers as in these positively charged beads associate with, and therefore, exchange with negatively charged counter ions and hence metal ions be extracted as their anions. In present study poly(4-vinylpyridine) based crosslinked poly(ionic liquid) has been used as anion-exchangers for the extraction of Ni^{2+} metal ions from the aqueous solution. The extraction of Ni^{2+} was done by way of changing it to $NiCl_4^{2-}$. There are a number of metal ions, which exist as anions in the NaCl solution (13). As nickel is a strong chloride ion acceptor and mainly exists as anion in the NaCl solution, therefore, it can be changed to anion by adding the NaCl solution. After it is changed to anion, it can be extracted from the solution by using anion exchanger. The nickel metal ions can be removed by using the cation exchanger. But one of the great problems in this process is the formation of nickel hydroxide in the cation-selective membrane. This type of problem was not encountered in the present method and hence, the novelty of the present method comes in. The extraction of Ni^{2+} metal ions was carried by using reported crosslinked poly(4-vinyl pyridine) based PILs having bioactive choline analogous group shown below (12).

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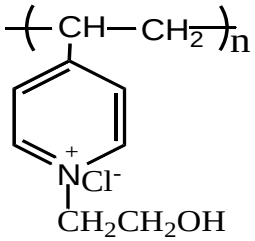

To have a series of crosslinked PILs the counter anion (Cl^-) of the prepared PIL was replaced with Br^-, OH^-, SH^-, NO_3, BF_4^- and CF_3COO^- by the simple metathesis reaction (12).

2. EXPERIMENTAL:

2.1. MATERIALS:

4-Vinyl pyridine (Merck, Schuchardt, Germany), nickel chloride (Merck, Schuchardt, Germany), benzoyl peroxide (S. D. Fine, Mumbai), ethylene glycol dimethacrylate (Merck, Schuchardt, Germany), 2-chloroethanol (S. D. Fine, Mumbai), NaCl, NaBr, NaOH, NaSH, $NaNO_3$, $NaBF_4$ and CF_3COOK were used as received.

2.2. SYNTHESIS OF ANION-EXCHANGERS:

PILs were prepared by the same method as reported in early publication (12) by taking known amount of 4-VP, 1% (by weight) initiator benzoy peroxide, 2% (by weight) crosslinker ethylene glycol dimethacrylate was added and polymerization was carried at 70 ºC in water bath for 2.5 h. The crosslinked network was washed with ethanol to remove any uncrosslinked polymer and then dried at 60 ºC. The quaternization reaction on poly(4-VP) network was carried out by taking poly(4-VP) and 2-chloroethanol in 1:5 weight ratio and heated at 50 ºC for 36 h to ensure maximum extent of reaction. The synthesized anion-exchanger was denoted as [Poly(4-VP-*cl*-EGDMA)-CH_2CH_2OH]$^+$ Cl^-. The unreacted 2-chloroethanol from the anion-exchanger was removed by washing with water and then dired at 60 ºC till constant weight was obtained. To get a series of new anion-exchanger, Cl^- was replaced by simple metathesis reaction using different anions as Br^-, OH^-, SH^-, NO_3^-, BF_4^-, and CF_3COO^-. 7 g each of NaBr, NaOH, NaSH, $NaNO_3$, $NaBF_4$, or CF_3COOK was dissolved in minimum amount of distilled water and 1 g [Poly(4-VP-*cl*-EGDMA)-CH_2CH_2OH]$^+$ Cl^- was added to each salts solutions and then was stirred for 6 h. Then networks were washed with distilled water and dried at 60 ºC till constant weight was obtained.

2.3. EXTRACTION OF NICKEL METAL IONS:

For the study of the extraction of nickel metal ions, 1000 ppm of Ni^{2+} metal ions solution was prepared in the 3M, 4M, 5M NaCl solution. The different reference curve was prepared for each NaCl concentration and the absorbance was taken on the UV-Visible spectrophotometer (Varian Cary-300) at 396 nm. The reference curve was drawn as absorbance vs. concentration of Ni^{2+} metal ions solution. 0.1g of different PILs were stirred with 20 mL of Ni^{2+} (1000 ppm) in 5M NaCl solution for 6h, which was followed by filtration and absorbance of the filtrate was taken at 396 nm. From the reference curve the concentration of Ni^{2+} metal ions in the filtrate was calculated. The PIL which showed maximum extraction of nickel metal ions was used in further studies. The nickel metal ions extraction was studied as a function of time by stirring 0.1g of PILs with 20 mL of Ni^{2+} (1000 ppm) in different NaCl (3M, 4M and 5M) solution for 30, 1h, 2h, 3h, 4h, 5h and 6h. The concentration of rejected Ni^{2+} metal ions in the filtrate was measured from the reference curve. The effect of temperature was studied by following the same for 6h at 20, 25, 30, 35, 40 and 45ºC. To find the maximum retention capacity (MRC) of anion exchanger, 0.1g of it was stirred for 6h with 20 mL of Ni^{2+} (1g/L) in 5M NaCl solution. The experiment was repeated many times using the same anion exchanger sample.

2.4. EXPRESSIONS USED:

The metal ions extraction efficiency of the PILs was expressed in percent by using following the relationships:

$$\text{Percent uptake } (P_u) = \frac{\text{Amount of metal ions taken by the PIL}}{\text{Total amount of metal ions in feed}} \times 100$$

3. RESULTS AND DISCUSSION:

3.1. SELECTION OF THE MOST EFFICIENT ANION EXCHANGER:

The maximum extraction of nickel metal ions was 60% and the PIL having Cl^- anions, showed the maximum uptake capacity (Fig. 1). The order of P_u by different PILs as [Poly(4-VP-*cl*-EGDMA)-CH_2CH_2OH]$^+$ Cl^- > [Poly(4-VP-

cl-EGDMA)-$CH_2CH_2OH]^+$ Br^- > [Poly(4-VP-*cl*-EGDMA)-$CH_2CH_2OH]^+$ NO_3^- > [Poly(4-VP-*cl*-EGDMA)-$CH_2CH_2OH]^+$ OH^- > [Poly(4-VP-*cl*-EGDMA)-$CH_2CH_2OH]^+$ SH^- > [Poly(4-VP-*cl*-EGDMA)-$CH_2CH_2OH]^+$ BF_4^- > [Poly(4-VP-*cl*-EGDMA)-$CH_2CH_2OH]^+$ CF_3COO^-.

3.2. STUDY OF EFFECT OF TIME, TEMPERATURE AND SODIUM CHLORIDE CONCENTRATION:

The extraction of nickel metal ions was slow and it increased with an increase in time and attained equilibrium at around 200 min. The P_u increased sharply in first two hours and thereafter, it remained constant in all NaCl concentrations. Metal ions extraction increased with increase in NaCl concentration and this trend supports that the formation of $NiCl_4^{2-}$ nickelate anion as it increases with the increase in brine solution concentration. When the concentration of NaCl was 3M the P_u was only 25.71, but when it was increased upto 5M the P_u increased to become 60.06 at 6h (Fig. 2). The effect of temperature on the P_u of nickel metal ions was very small. It remained almost constant when temperature was increased from 20ºC to 45ºC (Fig. 3) and some tendency of desorption can be understood with the increase of temperature. The MRC of the nickel metal ions extraction could not be calculated, as the PIL started desorption even after the first feed of metal ions solution.

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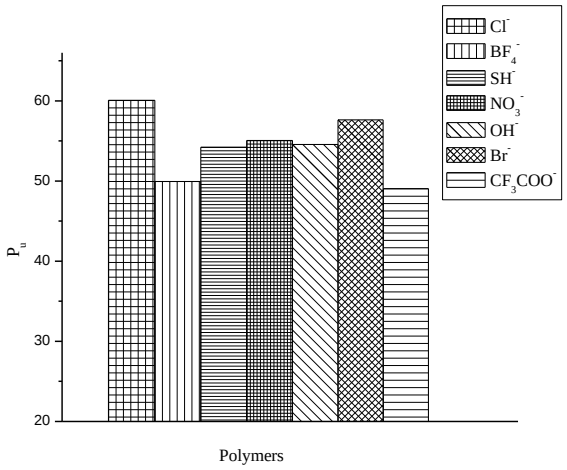

Fig. 1: Nickel metal ions extraction by the different PILs at 20ºC. (Time = 6h, [Ni^{2+}] =1000ppm, [NaCl] = 5M, Volume of solution = 20 mL)

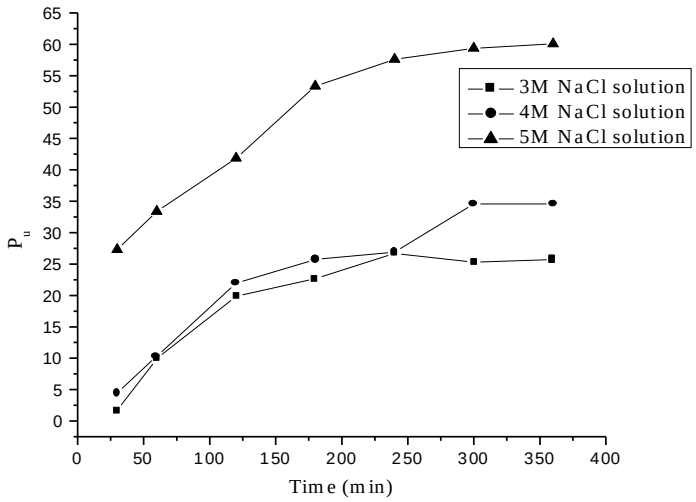

Fig. 2: Nickel metal ions extraction as a function of time at 20ºC. (Volume of solution = 20 mL, [Ni^{2+}] =1000ppm)

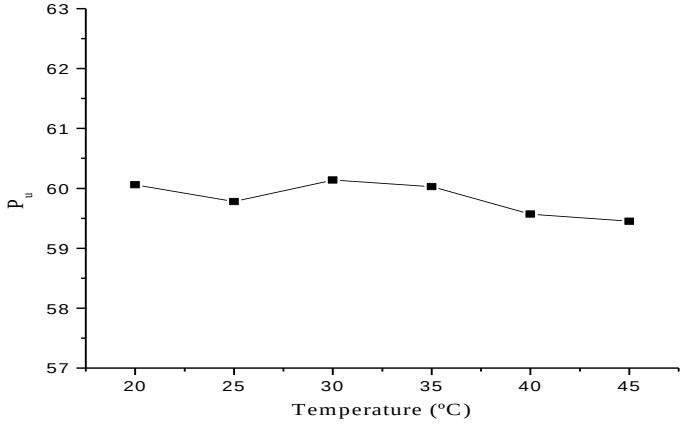

Fig. 3: Nickel metal ions extraction as a function of temperature. (Time= 6h, [Ni^{2+}] =1000ppm, [NaCl] = 5M, Volume of solution = 20 mL)