Study of The Influence of Inductive Groups on The Performance of Carboxylate-based Hydrogel Matrix

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Introduction

Presently, the utilization of hydrogel to collect valuable metal from liquid wastes or seawater has become promising from the standpoint of adsorption capacity with low metal ion concentration in aqueous solution (less than 50 mg/L) and cost-effective technologies. The efficiency of hydrogel is determined by two key factors: the adsorption efficiency of target-capturing functional group; and the matrix of hydrogel structure where the functional group is grafted. This discussion investigated the group functionality of hydrogels. Herein, we explored the role of matrix to the activity hydrogel behavior, especially by changing the electron density of the functional group. The study especially sought to estimate the influence of two groups: bromine (Br) and methyl group (CH_3), grafted onto the hydrogel matrix and their effect on the carboxyl function group towards Vanadium (V) adsorption capacity.

Experimental

Table I: Chemical compositions of studied hydrogels

Composition (%mole)	Hydrogel
100% NAc	100 NAc
5% BrAc; 95% Ac	5 Br
10% BrAc; 90% Ac	10 Br
15% BrAc; 85% Ac	15 Br
30% NMAc; 70% Ac	30 NMAc
50% NMAc; 50% Ac	50 NMAc
70% NMAc; 30% Ac	70 NMAc

The chemical compositions of the different hydrogels have been listed in Table I. Different hydrogel types were prepared from varying concentration ratios of Sodium methacrylate (NMAc)/Sodium acrylate (NAc) and 2-Bromoacrylic acid (BrAc)/Sodium acrylate (NAc). The monomers were dissolved and polymerized in dimethyl sulfoxide solvent and cross-linked using 40 mM of N,N'-methylene-bisacrylamide. Synthesized hydrogels were rinsed in pure water and cut into 0.5 g pieces. The amount of dry polymers in swollen hydrogel ranged from 0.1% to 0.5%. Other characterization included the FTIR spectroscopy.

Samples of 0.5 g of the swollen hydrogels were immersed in respective 25 mL V test solutions of 50 ppm each and pH = 2.1, to investigate adsorption for 2 days. Changes in metal concentration was monitored using an inductively coupled plasma mass spectrometry (ICP-MS).

Results and Discussion

In the FT-IR spectrum, the O-H and C=O stretching vibration at 2600-3500 cm^{-1} and 1500 cm^{-1} were observed, consistent with the carboxyl functional group. The intensity of 1000 cm^{-1} peak (assigned to CH_3 deformation bending vibrations) and 1700 cm^{-1} (due to overtone interaction of C=O stretching vibration by Br- group) was found to increase with CH_3- and Br- ratio, indicating CH_3- and Br- group incorporation into the hydrogels matrix.

Results of V adsorption on each hydrogel (Table I) performed under the same experiment conditions are summarized in Fig. 1. It can be seen that xBr hydrogel had the greatest adsorption performance while yNMAc hydrogel was lowest. Comparing with the base case 100NAc hydrogel without inductive group, the adsorbed V amount consistently increases with the ratio of Br- and decreases with the ratio of CH_3-. This phenomenon possibly occurs because the more electronegative Br- group will increase the positive charge on hydrogen of the carboxyl function group by greater withdrawal of electron density on the hydrogel matrix. Consequently, the O-H bond become weaker, enabling easy release of H^+ for ion exchange.

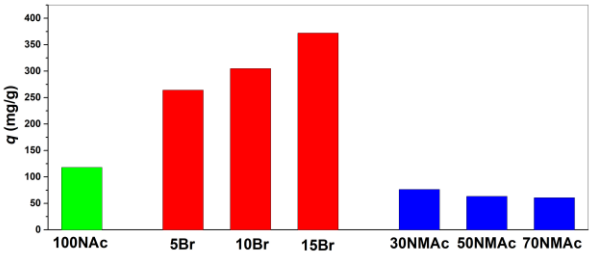

Fig. 1. Adsorption capacity of Vanadium onto xBr and yNMAc hydrogel.

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