International Journal of Multidisciplinary Research and Development
Online ISSN: 2349-4182, Print ISSN: 2349-5979; Impact Factor: RJIF 5.72
Received: 23-01-2020; Accepted: 24-02-2020; Published: 25-03-2020
www.allsubjectjournal.com
Volume 7; Issue 3; 2020; Page No. 129-132

Removal of copper (II) and vanadium (V) from their aqueous solutions using hydroxamated polyacrylamide resin

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Abstract

Hydroxamated poly acrylamide (HPAAM) was prepared by coupling reaction of polyacrylamide (PAAm) and free hydroxylamine in alkaline solution (pH>12) at 70˚C. The HPAAM were characterized by CHN elemental analysis and Fourier-transform infrared spectroscopy (FTIR). The results of CHN elemental analysis have demonstrated that HPAAM composes of 29.71% carbon, 4.08% hydrogen and 12.66% nitrogen. Characteristics absorption bands of HPAAM functional groups at 3300-3600cm^{-1} (OH), 1666 cm^{-1} (C=O) and (N-H) 3211 cm^{-1} were noticed from FTIR spectra. Furthermore, the removal capacities of HPAAM for copper and vanadium ions were investigated by batch technique at various pH values. The results revealed that the uptake of copper (II) achieves a value of 97.29 % at pH 5 while for vanadium (V) it is 97.08 % at pH 2 after 24 hours equilibration.

Keywords: batch technique, bidentae, chelating resin, uptake

1. Introduction

Contamination of water resources by heavy metals has become one of the challenging issue globally due to their hazardous effects to both human being and ecological system [1, 2]. Chelating resins have received considerable attention in the removal of harmful trace metal ions because of their high selective bonding capacity for heavy metal ions. There are many types of chelating ligands that have been reported for the binding of metal ions [3-6]. Consequently, poly (hydro xamic acid) and poly (amidoxime) are well known chelating resins that bind the wide metal ions in the presence of alkali metal ions. Poly(hydroxamic acid) was prepared from poly(methyl acrylate) grafted sago starch and the binding capacities of copper, iron, chromium, nickel, dysprosium, gadolinium and uranium were found excellent; other metal ions have significant sorption capacities [7]. Depending on the pH, hydroxamic acids react with metal ions in different stoichiometric ratios [8].

A number of methods have been used for the removal of these metals from wastewater; the ordinary methods are precipitation, ion exchange and reverse osmosis, coagulation and flocculation, membrane separation, biosorption, and adsorption [9, 10]. These methods have significant disadvantages, including high energy requirements, inefficient metal removal, generation of toxic sludge, and expensive equipment. hence, there is a need to develop an competent, express, cost-effectively and environment friendly method for the removal of heavy metals from effluents. Adsorption of heavy metals is a new technology for treatment of material effluents containing different types of heavy metals. Adsorption is the adhesion of a chemical substance (adsorbate) onto the surface of a solid (adsorbent). The most widely used adsorbent is activated carbon [11]. The adsorption process is being widely used by various researchers for the removal of heavy metals [12–17].

Batch extraction the simplest and most commonly used method, consists of extracting the solute from one immiscible layer into other by shaking the two layers until equilibrium is attained, after which the layers are allowed to settle, then the successive extraction were performed. This is commonly used on the small scale in chemical laboratories [18]. Batch extraction experiments were used to compare the Complexing ability of the hydro xamic acid resins [19].

The present study aimed to investigate the ability of hydroxamated polyacrylamide (HPAAM) as a potential chelating resin for removal of copper (II) and vanadium (V) from their aqueous solutions at various hydrogen ion concentrations.

2. Materials and Methods

2.1 Chemicals

Hydroxamated polyacrylamide (HPAAM) was previously prepared by coupling reaction of polyacrylamide (PAAm) and free hydroxylamine in alkaline solution by Nehal, El mugdad and Ahmad [20]. Hydrochloric acid, sodium hydroxide pellets, copper sulphate pentahydrate, methanol and ammonium chloride were all purchased from LOBA Chemie (India). Ammonium metavanadate was obtained from CDH (China). All chemicals used were of AR grade and were used directly without further purification.

2.2 Instruments

2.2.1 UV/Visible spectrophotometer Model 7205, Jenway, England.

2.2.2 Thermo Nicolet IR/300 Spectrophotometer in the range (400-4000) cm^{-1} using KBr disc, USA.

2.2.3 Vario MACRO cube Elemental analysis, CHNS/O analyzer, syntpot oü, Tartu, Estonia.

2.2.4 Atomic Absorption Spectrometer Savant AA, GBC Scientific Equipment Pty Ltd, GBC, A 7804, Australia.

2.3 Methods

2.3.1 Preparation of stock solution of metals

A stock solution having 1000 ppm concentration of copper was prepared by weighing accurately 1.98 g of $CuSO_4.5H_2O$, dissolved in distilled water, transferred into 500 cm^3 volumetric flasks and completed up to the mark with distilled water.

A stock solution having 1000 ppm concentration of vanadium was prepared by weighing accurately 1.14g of NH_4VO_3, dissolved in distilled water, transferred into 500 cm^3 volumetric flasks and completed up to the mark with distilled water. Then a dilute solution having 100 ppm concentration was prepared from the 1000 ppm stock solution.

2.3.2 Sorption of metals ions using the batch technique

To study the influence of pH on sorption capacity of copper (II) and vanadium (V), a series of experiments were conducted at pH range 1, 2, 3, 4, 5, 6. The pH was adjusted to appropriate value pH (1-2) using potassium chloride in hydrochloric acid and pH (3–6) using sodium acetate buffer (10 cm^3). In a typical experiment, exactly 0.150 g of the HPAAM was added to 10 cm^3 of a metal ion solution (1000 ppm) and shaked well for 30 min with speed of 180 rpm. After equilibration, the solid was separated by filtration and copper (II) ion concentration was determined by atomic absorption spectrometer [19, 21]. The sorption capacity of vanadium (V) was studied following typical steps as for copper (II) but the concentration of vanadium (V) solution was 100 ppm and the remaining concentration of the vanadium ion was determination by UV/Visible Spectrophotometer. The initial and final readings (after adsorption) of the metal ion concentration were calculated according to the following equation

$$\text{Adsorption (\%)} = \frac{(C_o - C_t)}{C_o} \times 100$$

Where

C_o is the initial concentration of metal solution (mg l^{-1})

C_t is the equilibrium concentration of metal (mg l^{-1}) after adsorption

3. Results and discussion

3.1 Color test and CHN elemental analysis

Color tests of HPAAM with copper (II) and vanadium (V) were conducted to confirm the availability and the ability of hydro xamic acid functional groups to bind to the above metals. The results have shown the presence of characteristics dark green and dark purple colors of these metals/HPAAM complexes respectively. The yield and the CHN elemental analysis of HPAAM are shown in Table 3.1.

Table 1: The yield and the elemental analysis of hydroxamated polyacrylamide.

Sample	Yield (%)	Color	C (wt %)	H (wt %)	N (wt %)
HPAAM	54.65	white	29.71	4.08	12.66

3.2 Fourier transform infrared spectroscopy (FTIR)

The infrared spectrum of the crosslinked HPAAM resin showed the presence of the characteristics absorption bands of symmetric and asymmetric $–CH_2$ stretching and C-N stretching at (2928, 2850) and 1400cm^{-1}. However, the absorption band of hydro xamic carbonyl group has shifted to 1666 cm^{-1} and the N-H stretching as well as the –OH group stretching vibration were both appeared as a broad band in the range between 3100 - 3500 cm^{-1}.

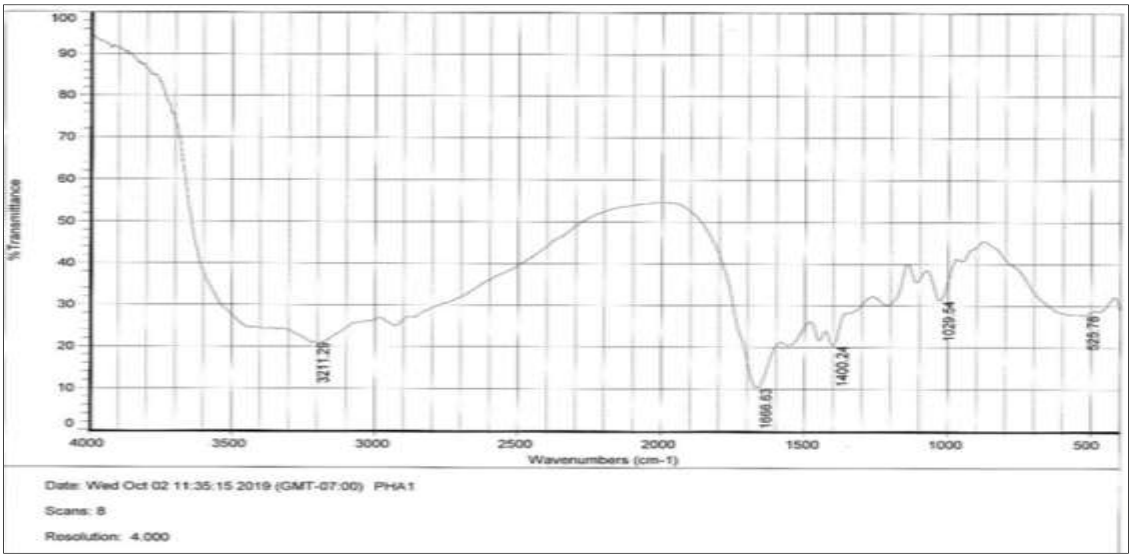

Fig 1: FT-IR spectrum of HPAAM

3.3 Sorption of metal ions using the batch technique

The results of batch extraction experiments which were used to compare the complexation ability of the hydroxamated polyacrylamide with copper (II) and vanadium (V) were shown in Figures 3.2 and 3.4. Figure 3.2 shows the dependence of copper ion extraction efficiency on the pH of the metal ion-aqueous solution in the range between 1 and 6. It could be noticed from Figure 3.2 that there is a gradual increase in the extraction efficiency with increasing pH from 1 to 4 then there was a steep increase that starts at pH 4 and reaches it is maximum at pH 5 which followed by a sharp decrease. At pH 5 the uptake of Cu (II) achieves a value of 97.29 % after 24 hrs equilibration. It is worth noting that even at pH 1 and 24 hours of equilibration the removal efficiency of copper ion reached 96.4% which did not vary much from that one at pH 5, 97.29%. This result demonstrated that the pH from 1 to 5 could be suitable for copper ion removal. This variation in binding ability to HP

AAm at different pH values could be interpreted by the nature of chelating sites in the polymer. In HPAAM the oxygen of hydroxy group and the one for carbonyl group are both participated in complex formation. Hence varying the pH clearly influences their acid-base equilibria, which results in shifting the relative concentrations of the protonated and the unprotonated forms.

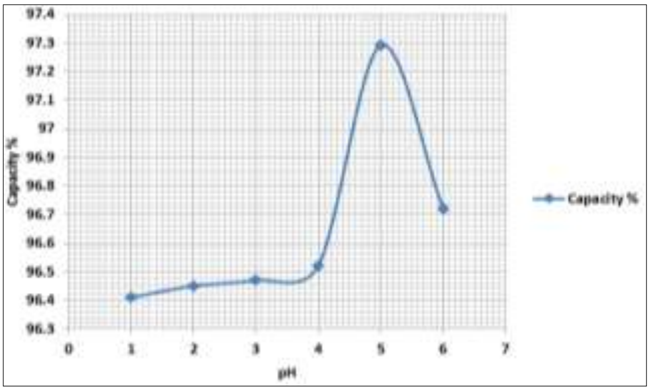

Fig 2: Effect of pH on the uptake of Cu (II) ions at room temperature and 24 hours equilibration time.

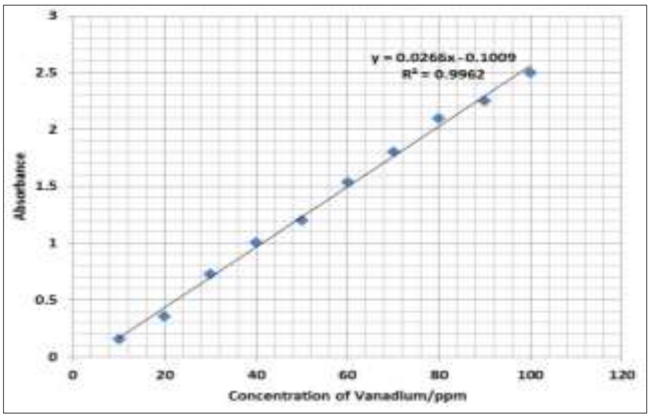

Fig 3: Calibration curve for standard solution of vanadium at λ_{max} = 234 nm

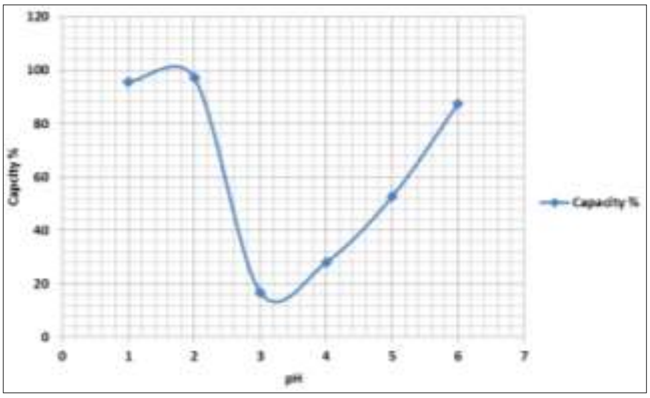

Fig 4: Effect of pH on the uptake of V (V) ions at room temperature and 24 hours equilibration time.

Figure 3.4 shows the dependence of vanadium ion removal capacity on the pH in range 1 to 6. The initial and final concentrations of vanadium ion were determined using UV/Visible Spectrophotometry. It is obvious from Figure 3.4 that the removal capacity increases from pH 1 to 2 gradually and reaches its maximum value at 2 (97.08%). Subsequently a sudden decrease was noticed at pH 3 (16.93%). Furthermore, the removal capacity increases again above pH 3 up to 6 (87.50%). These results show that the removal capacity of vanadium ion is greatly influenced by pH variation and could be achieved at low pH 1-2 as well as around 6.

4. Conclusion

Hydroxamated poly acrylamide (HPAAM) was successfully prepared and its metal binding properties were studied. It shows excellent adsorption capacities for copper (II) and vanadium (V) ions at different pH values. This type of resin has potential application for metal separation and recovery and it exhibits particular selectivity for metal ions at different pH values.

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