



Removal of Zirconium ions using Polymeric Adsorbent

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Abstract

Zirconium (IV) ions were removed from aqueous solutions by using amidoximated polyacrylonitrile and effect of different adsorption parameters like solution pH and contact time were also investigated. Also the products were characterized using XRD and FTIR analysis to study the adsorbent features. The FTIR graphs illustrate that change reveals an increment in –OH group of AMP, a suitable ligand for adsorption process. Zirconium peaks cannot be detectable in concentrations below 1000 ppm. Also, the initial faster rate may be due to surface adsorption. In the initial stage the surface was free and the reaction proceeded at a faster rate. Results showed that pH had strongest effect on adsorption capacity and maximum adsorption capacity obtained at pH=2 and the maximum adsorption capacity of Zr (IV) was 199.8 mg.g⁻¹, achieved at 318 K.

Keywords: Amidoximated polyacrylonitrile, Heavy metals, Zirconium, Adsorbent

1. Introduction

Nowadays developments of global industries increased demands for metal usage, and as a result, contamination of water resources is inevitable. Heavy metal ions such as copper, zirconium, iron, lead, zinc are not biodegradable and can make some dangerous environmental problems for human beings and other creatures. Thus, removal of heavy metals from waste waters have become one of the most important environmental issues in worldwide [1]. Zirconium is one of the most useful elements through the world and is used in different industries such as photoflash bulbs, ceramic industry, heavy metal adsorbents, glazes, surgical equipment, and so on. Therefore research on the treatment of waste waters which was contaminated by zirconium is also essential. Currently different methods have been employed to remove metal ions from aqueous solutions: membrane technology, liquid-liquid extraction, ion exchange chromatography, biosorption, adsorption, precipitation and so on [2] but they do not always sufficiently removed pollutions to have proper contamination control limits [3]. Lots of studies have been carried out for waste water treatment using different adsorbents like activated carbons, zeolites, alumina, and so on. Most of these materials deal with some problems like low stability, low removing efficiency, high cost, and so on [4]. The efficiency



of adsorbents in metal ions removal strongly depends on its functional groups. Polymeric materials which have some specific functional groups like phosphoric, amino or amidoxime have good ability to adsorb metal ions from contaminated solutions by forming strong complexes [5]. Consequently, some investigations focused on presence of nitrogen based ligands like amino, imidazole, and amidoxime on adsorbents and revealed that these chelating materials, which are insoluble in water, have superb adsorption characteristics and showed selective adsorption for some heavy metal ions. Amidoxime group has two superb types of functional groups on its surface: carboxyl and amino [6]. Therefore, it is expected that amidoxime should have excellent adsorption ability in heavy metal removal processes. Besides, acrylonitrile has been identified as a suitable polymer for waste water treatment. Some studies investigated on the efficiency of the acrylonitrile, and showed that amidoximated poly acrylonitrile has sufficient ability for removal of heavy metal ions [7]. Huang et al. produced amidoxime poly acrylonitrile (AMP) chelating nanofibers to adsorb iron and copper ions from aqueous solutions by electrospinning method. Results revealed that the conversion of nitrile groups into amidoxime group of PAN increased with reaction time, concentration of hydrochloride hydroxylamine and temperature. In order to enhance stability of samples, various methods have been applied to graft polymerization of acrylonitrile (AN) [8]. Reactions were carried out to amidoximation with hydroxylamine and were initiated by techniques like high energy radiation, UV, plasma radiation, ozonization or photopolymerization. Results showed that percentage of graft yield could reach to more than 60 % and amount of nitrile group which converted to amidoxime group could reach to about 2 mmol.g⁻¹ [9]. Therefore AMP showed optimistic behavior for removal of heavy metals but no report was focused on performance of them on removal of Zr ions from aqueous solutions. It is believed that a comprehensive study on the effect of different variables such as solution pH, contact time, temperature, adsorbent dose to solution volume ratio, and reflux time on the adsorption properties of Zr (IV) into AOP give a bright understanding for application of adsorption process in further waste water treatments. Therefore it is the aim of this research to investigate the adsorption properties of modified commercial PAN treated with hydroxylamine hydrochloride. This work deals with the investigation of the optimum separation and recovery conditions of zirconium as a function of initial zirconium concentration, pH, shaking time and temperature. Adsorbents amidoximated PAN were analyzed using FTIR and XRD.

2. Experimental

2.1. Chemical and Reagents

All chemical and reagents used in this study were of analytical reagent grade (AR grade). Deionized water was used to prepare all solutions. Solutions of zirconium oxy chloride octahydrate, ZrOCl₂·8H₂O (M_w=322.28g.mol⁻¹), from Romil company was used as the metal stock solution. Initial pH values of the metal solutions (1000 ppm) were about 1.3 and the desired pH were adjusted by adding hydrochloric acid or sodium hydroxide. The prepared PAN is the copolymer of acrylonitrile (94%) and methylacrylate (6%), with respectively numerical and weight average molecular weight of 70000 and 100000, were bought from Poly Acryl Company, Iran. For producing the amidoximated adsorbent, a solution of sodium hydroxide was added dropwise to the solution of 3 %vol hydroxylamine hydrochloride in methanol/water (50/50) to neutralize the HCl in the NH₂OH·HCl solution and the pH was kept at approximately 7. After the mixture was sufficiently stirred (~1h), mild sodium chloride precipitation was filtered. Amidoximated groups were introduced to the prepared PAN by treatment with hydroxylamine-alcohol solution at 80°C for 2h under reflux condition. The



obtained polyacryl amidoxime was washed with deionized water to remove excess hydroxylamine and finally dried at 70°C for 6h.

2.2. Equipment

A GFL shaker incubator was used for shaking the solution at desired temperatures; pH measurements were carried out using a Metrohm 746 pH-meter; the infrared spectra were measured by the KBr disk method using a Perkin-Elmer spectrometer and ICP-AES system, was used for measuring the trace elements after the batchwise procedure. X-ray diffraction (XRD) patterns were taken by Bruker, D8ADVANCE X-ray diffractometer.

3. Results and Discussions

3.1. Fourier transform infrared spectroscopy (FTIR)

The FTIR analysis was carried out with Perkin-Elmer instruments, Germany. The IR spectra of the chelate were similar to those of its ligands except that the intensity of bands decreases due to the amide and hydroxyl groups (Figure 1). This was attributed to the decrease in the dipole moment of amide and hydroxyl groups as a result of electron donation on the metal ion from the oxygen and nitrogen atoms of amidoxime groups. The appearance of absorption bands at 1650.46 and 941 cm^{-1} were attributed to -C=N- and =N-O- of the AO groups, respectively. In addition the increase in the absorption band around 3300-3600, compared to IR spectrum of the unmodified polymer, indicated the presence of -OH bonds that belongs to AO groups. These changes indicated that the modification reaction was successfully done. Appearance of a new band at 1204 cm^{-1} arises from alkoxy group which is characteristic for -O-M- band due to the complexation of AMP with Zr^{4+} through amidoxime group. As shown in Figure 1, by increment of reflux time, peaks of -OH groups tends to peaks of cyano groups in 2244 cm^{-1} . This change reveals an increment in -OH group of AMP, a suitable ligand for adsorption process

The conversion of nitrile group in the structure was calculated as follow:

$$C_n = \frac{A_0 - A_t}{A_0} \quad (1)$$

Where C_n is the percent of conversion and A_0 and A_t are the areas of $\text{C}\equiv\text{N}$ bands observed at 2240 cm^{-1} before and after amidoximation time t , respectively.

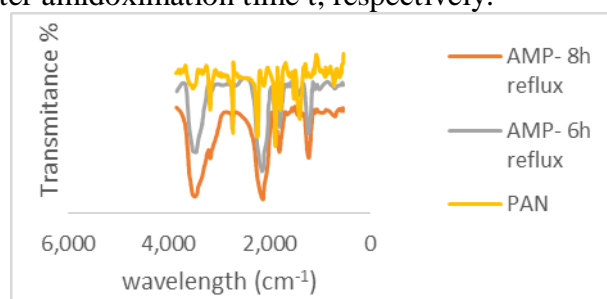


Figure 1. FT-IR spectra of PAN, AMP; 6 h reflux, AMP; 8 h reflux, and AMP-Zr complex, “adsorbent dose: 0.5 gr, pH = 1.3, contact time: 45 h, Zr concentration: 1000 ppm, solution volume: 15 cc, temperature = 25 °C

3.2. XRD analysis

XRD results for adsorbent before and after adsorption process respectively are shown in Figures 2 and 3. Nevertheless Zirconium peaks are observable in XRD pattern, Zirconium adsorption onto AMP has not change ligand pattern, which boost this idea that Zirconium ions were taken in AMP structure in the same phase. Metal-polymer complex is not a crystal, so its



structural studies were not accurately feasible. Main peaks of Zirconium are detectable in $2\theta = 36, 35, 32.48, 5, 69$, which peaks in 36 is more intense than others. This reveals that due to low concentration of Zirconium change in crystallinity of adsorbent is not observable. Overall unlike Zeolite which has crystal structure, peer assessment of Zirconium peaks by XRD test is not so applicable. Zirconium peaks cannot be detectable in concentrations below 1000 ppm.

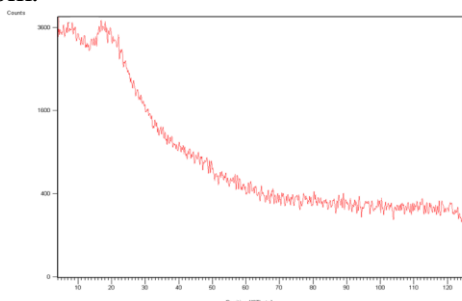


Figure 2. XRD patterns of modified polymer before adsorption; adsorbent: 0.5 gr, solution volume: 2.15 ml, T=45 °C

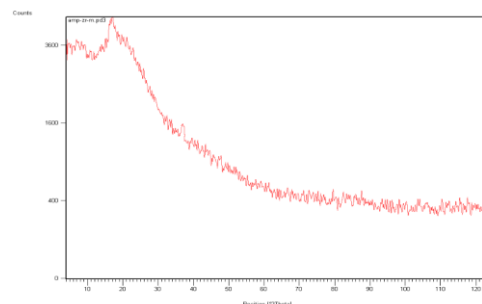


Figure 3. XRD patterns of modified polymer after adsorption; adsorbent: 0.5 gr, solution volume: 2.15 ml, T=45 °C;

3.3. Effect of contact time

The effect of contact time on zirconium adsorption was studied in zirconium solution with concentration of 100 ppm and mass to volume ratio of 1:150 at 25 °C. The initial pH was 1.3. The results are shown in Figure 4. It is obvious from the slope of the curve that adsorption rate was fast at the beginning and became slow with the progress of the reaction. The initial faster rate may be due to surface adsorption. In the initial stage the surface was free and the reaction proceeded at a faster rate. First the available free surface was clogged; the adsorbed molecules penetrated through the pores and get adsorbed inside the pores which are known as intra-particle diffusion. In the Figure 4, the relationship between Zr adsorbed (on the base of adsorbent weight) and the time was shown.

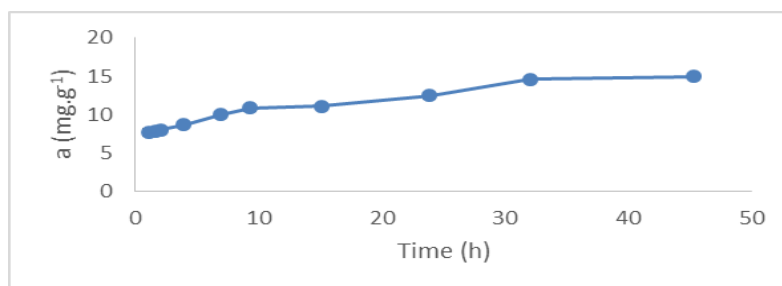


Figure 4. Effect of contact time, “adsorbent dose: 0.5 gr, pH = 2, Zr concentration: 100 ppm, solution volume: 15 cc, temperature = 25°C

3.4. Effect of initial pH

Zirconium has a controversy and remarkable pH behavior. Many studies have been done on aqueous solution chemistry and hydrolytic polymerization of aqueous zirconium ions [10]. The onset of zirconium hydrolysis occurs in strongly acidic conditions ($\text{pH} < 0$) and is dominated by the formation of polynuclear species. The onset of precipitation reactions also occurs at low pH values (~ 2) and these features have made the hydrolysis and solubility of this cation difficult to study. Walther et al investigated polynuclear species of zirconium in acidic aqueous solutions by combining X-ray absorption spectroscopy (XAFS) and nano-electrospray mass spectroscopy (ESI-MS). Species distributions were measured at $0 < \text{pH}$



< 3 , $[Zr] = 1.5 - 10 \text{ mmol.L}^{-1}$ [11]. While the monomer remains as minor species, with increasing pH the degree of polymerization increases and the formation of tetramers, pentamers, octamers and larger polymers are observed. Zirconium ion (Zr^{4+}) is stable only under very acidic conditions ($pH < 0$), and that mononuclear hydroxide complexes dominate only in very dilute solutions ($[Zr] < 10^{-5} \text{ mol.L}^{-1}$). At higher concentrations or lower acidities, the solvated (Zr^{4+}) ion ($Zr^{4+} \cdot 8H_2O$) hydrolyzes and forms ($Zr(OH)^{3+} \cdot 7H_2O$) and ($Zr(OH)_2^{2+} \cdot 6H_2O$). The low adsorption capacity obtained for different forms is attributed to the formation of these species [12].

The pH value is an important factor in the use of polymers for metal ion adsorption process. It is not only affecting the electronic status of the pendant functional groups or dissociation/association of acidic groups, but it may also alter the oxidation forms of the metal ions present in the aqueous media. As expected, the higher acidic condition, results the lower adsorption of metal ions. This may be due to the protonation of the amino groups at the acidic conditions. The zirconium concentration depends severely on the pH of the solution. In this paper, the adsorption property of AMP was investigated at ($pH \sim 1-4$). Experiments showed that further increase of pH would result in the hydrolysis and precipitation of (Zr^{4+}). It could be obviously observed in Figure 5 that the pH value of the solution had only a slight effect on the adsorption of AMP. As seen, AMP beads had good adsorption for (Zr^{4+}) among a wide range of pH values ($pH=1-4$). This may be due to oxygen and nitrogen atoms, the main contributors for chelating (Zr^{4+}) that could not be protonized under this experimental condition. Finally, the $pH=2$ has been chosen for all experiments.

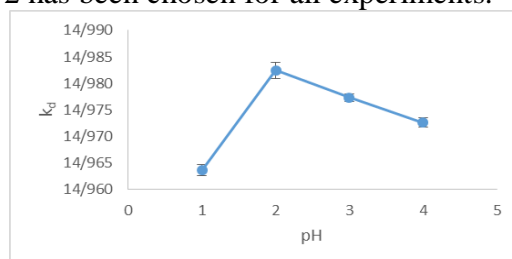


Figure 5. Effect of the solution pH on zirconium adsorption, “adsorbent dose: 0.5 gr, contact time: 45h, Zr concentration: 100 ppm, solution volume: 20 ml, temperature = 25°C

Results show that maximum amount of metal uptake capacity (adsorbed ion (mg)/dry adsorbent (g)) for current research reach to about 199.8 mg.gr^{-1} while this value for adsorption of zirconium onto living and dried biomasses of *Aspergillus niger* was 78.8 mg.gr^{-1} and 142 mg.gr^{-1} , respectively [13]. Akhtar et al. showed that maximum uptake capacity of zirconium for *Candida tropicalis* biosorbent reached to 179 mg.gr^{-1} but more slower than other researches [14]. Furthermore study of Bhatti et al. [15] revealed that maximum uptake of zirconium in to *Coriolus versicolor* biosorbent could reach to about 71 mg.gr^{-1} . Faghihian et al. [16] revealed that in case of modified clinoptilolite adsorption capacity was 1.46 meqg^{-c} . By concentration on the effect of pH on adsorption process in current research and other relevant ones, it was found that process was highly dependent on initial pH. Adsorption capacity increased by pH for *Coriolus versicolor* and *Aspergillus niger* while in our research it reached to a maximum value in $pH=2$ and then decreased in upper pH values. Optimal pH in adsorbents of clinoptilolite and *Aspergillus niger* was $pH=1$ and $pH=3.1$, respectively.

4. Conclusion

Chemically modified AMP as a sorbent has been proposed to be an efficient alternative in removal of Zr cation from aqueous solutions. Batch sorption studies of zirconium ions showed



that AMP could be successfully used to remove Zr ions from aqueous solutions (199.8 mg.g⁻¹).

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