Adsorption features of modified Polyacrylamide and its application in Water Treatment

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Abstract: In this study the adsorption of iron, and cadmium by modifying polyacrylamide was investigated. Amino groups have been introduced to enhance the activity of polyacrylamide using ethylenediamine. Metals uptake results showed that, high adsorption rates at the beginning of measurements followed by adsorption equilibrium, which is gradually reached within 100 min. The effect of the PH on the adsorption process was also investigated. Results showed that, changing the pH value from the normal case 1.5 to higher value 7, has increased the adsorption rates of the metals, so higher metals uptake were gained.
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1. Introduction

Increasing the activity of polymeric materials by introducing different functional groups has attracted high interest recently **(Kenawy et al., 1998).** In this context, removal of heavy metals using chelating polymers have been reported extensively **(Al-Qahtani, 2012; El-Toony, 2011; Beatty et al., 1999; Chen et al., 1999; Amoaw et al., 2009; Bessbousse et al., 2012; El-Dessouky et al., 2012).** Heavy metals are released into the environment in a number of different ways, and affect ecological life owing to their tendency to accumulate in living organisms and their acute and long term toxicity **(Fu & Wang, 2011)**.

These Heavy metals are found in a variety of industrial wastewater, including planting, chemical, fly ash, blast furnace slag, petrochemical, sludge paint and pigment manufactures as well as most others to a lesser extent **(Ahmaruzzman, 2011).** Heavy metals such as mercury, lead, copper, arsenic and cadmium are highly toxic metals when absorbed into the body **(Denizli et al., 2000)**. "They represent a major hazardous waste in the environment since they can be taken into the body through the pulmonary system from the contaminated air or cigarette smoke or via the digestive system through water or food contamination from plant metal uptake" **(Sağlam et al, 2001; Al-Saleh et al., 2011; Jin et al., 2013)**. The presence and accumulation of heavy metals in the human body may cause accumulative poisoning, cancer, brain damage…,etc **(Hutton & Symon, 1986; Khlifi et al., 2013)**.

In this study we report the modification of Polyacrylamide by grafting with ethylene diamine. And examine the produed modified compound for the removal of Fe (III), and Cd(II) from water under equilibrium conditions.

2. Material and Methods

1.1 Materials:

Polyacrylamide (PA), Ethylenediamine (EDA), Absolute methanol, Iron(III)nitrate(1N), and Cadmium(II)nitrate (1N) were purchased from Aldrich, U.S.A.

Experimental:

1.1.1 Modification of polyacrylamide (P 1) with ethylenediamine:

In atypical procedure (Kenawy et al., 2006), 42.3 g of Ethylenediamine in 50 ml methyl alcohol, 5 g of poly acrylamide (P1) was added stepwise with stirring in 250 ml round bottled flask. After the addition was completed, the system was fitted to reflux at 80 oC for two days with continuous stirring. The modified polyacryamide (P2) was filtered off, washed five times with methyl alcohol to remove the unreacted ethylenediamine. The product (P 2) was collected as a white powder and dried in vacuum oven at 40 oC overnight. The yield was 4.557 g (56.75 % yields) as a white powder (cf. Scheme 1).

The product was characterized by elemental microanalysis and IR spectroscopy. This modified polymer was used in metal adsorption studies. Also, the product was characterized by X-Ray Diffraction pattern and DTA. TGA analyses for the modified polymer were obtained before and after gamma radiation to study the effect of radiation on the prepared polymer.

1.1.2 Iron (III) adsorption studies:

25 ml of aqueous solutions containing 6 mg / l of Fe+3 nitrate were treated with 6 mg of the polymer under study (8 Polymers were used for this study), (at pH of 2.5 " adjusted with HNO3 – NaOH " at the beginning of the experiment and not controlled afterwards) at room temperature, in flasks with stirring. The concentration of Fe+3 ions in the aqueous phase, after the desired treatment periods (20, 40, 60, 80, 100 min) was measured by using an atomic absorption spectrophotometer at a wavelength of 248.3 nm. The instrument response was periodically checked with a known metal solution standards which is Fe+3 - nitrate (2, 4, 8 ppm). This application was done at different pH values 1.5, 2.5, 7 and 11 to study also the effect of pH value on the amount of the metal adsorbed on the polymer. The adsorption rates of Fe(III) by the polymers at the concerned pH value are plotted as shown in figures 5, and 6.

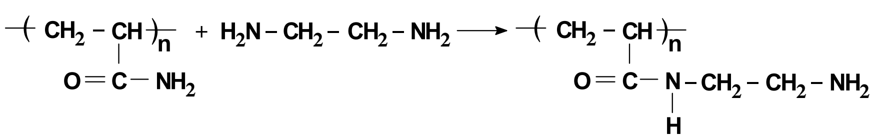
1.1.3 Cadmium (II) adsorption studies:

25 ml of aqueous solutions containing 6 mg / l of Cd+2 nitrate were treated with 6 mg of the polymer under study (8 Polymers were used for this study), (at pH of 2.5 " adjusted with HNO3 – NaOH " at the beginning of the experiment and not controlled afterwards) at room temperature, in flasks with stirring. The concentration of Cd+2 ions in the aqueous phase, after the desired treatment periods (20, 40, 60, 80, 100 min) was measured by using an atomic absorption spectrophotometer at wavelength of 228.8 nm. The instrument response was periodically checked with known metal solution standards Cd+2 nitrate (2, 4, 8 ppm.). This application was done at different pH values 1.5, 2.5, 7 and 11 to study also the effect of pH value on the amount of the metal adsorbed on the polymer. The adsorption rates on Cd(II) by the polymers at the concerned pH value are plotted as shown in figures 7, and 8

3. Results and Discussion

1.1 Materials Characterization:

The modification of the polyacrylamide with ethylenediamine was carried out to improve the activity of the polyacrylamide by introducing free amino group. The amine modified product polymer 2 (P2) and also the main substance polyacrylamide (P1) were characterized by elemental analysis, IR-spectroscopy and TGA analysis. The product and the main polymer were applied to study the adsorption of metals from solutions.



Polyacrylamide Ethylenediamine Modified Polyacrylamide (MPA)

P 1 P 2

Scheme 1: Modification of polyacrylamide (p1) with ethylenediamine

The elemental analysis for P1 and P2 are as shown in Table (1). It seems in a good agreement with the calculated values.

Table 1. Elemental microanalysis for polymers.
Calc.* = Calculated %

Polymer code	C %		H %		N %	
	Calc.*	Found	Calc.	Found	Calc.	Found
P1	50.7	49.46	7.04	7. 7	19.24	18.57
P2	52.63	50.91	8.77	8.07	24.56	22.76

Figure 1 shows the IR spectrum of P1, the peak at 3400 cm-1 indicate the presence of stretched amine -NH, the peak at 1650 cm-1 indicate the presence of stretched amide group (-C = O), also, stretched C-H was indicated by the peak at 2900 cm-1. The IR spectrum of P2, figure 2, shows a peak at 3500 cm-1 which indicate the presence of stretch amide -NH that indicate the formation of the condensation reaction. The peak at 1650 cm-1 indicate the presence of stretched amide group (-C = O). Also, stretched C-H was indicated by the peak at 2900 cm-1.

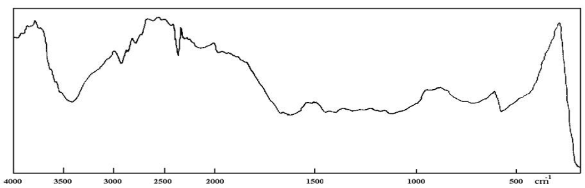


Figure 1: The IR spectrum of Polyacrylamide

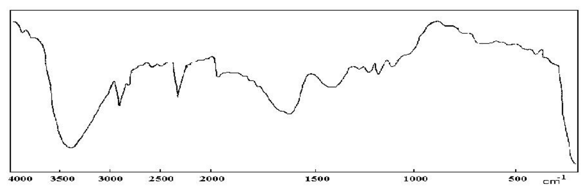


Figure 2: The IR spectrum of modified Polyacrylamide

The TGA thermogram in a nitrogen atmosphere for polymer 1 (P1) is shown in figure 3. It is suggested that in the initial stage of thermogram the weight loss at 31.07 - 86.98 °C is due to the loss of humidity water contained in a such hydrophilic polymer, and the weight loss at 88.37 - 233.62 °C is due to the loss of the water of crystallinity. At the second stage 235.52 - 555.42 °C, the weight loss is due to the loss of the side groups and branches of the polymer. However, at the third stage 556.86 - 638.20 °C, "the weight loss may be due to the main chain scission in the polymer chain and matrices. Heating the polymer to higher temperature than 638.20 °C, results in rapid decomposition to carbon oxide and volatile hydrocarbons" **(Abd El-Aal et al., 2005).**

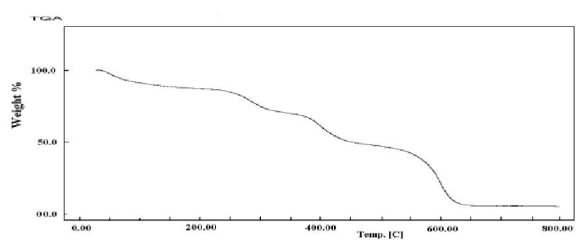


Figure 3: TGA Thermogram of Polyacrylamide

Figure 4 shows the TGA thermogram in nitrogen atmosphere for polymer 2 (P2). It is suggested that in the initial stage of thermodiagram the weight loss at 23.05 - 102.20 °C is due to the loss of humidity water content, and the weight loss at 102.20 - 202.54 °C is due to the loss of the water of crystallinity. At the second stage 203.56 - 437.61 °C, the weight loss is due to the loss of the side groups and branches of the polymer. However, at the third stage 438.17 - 674.35 °C, "the weight loss may be due to the main chain scission in the polymer chain and matrices. Heating polymer at higher temperature than 674.35 °C results in rapid decomposition to carbon oxide and volatile hydrocarbons" **(Abd El-Aal et al., 2005).**

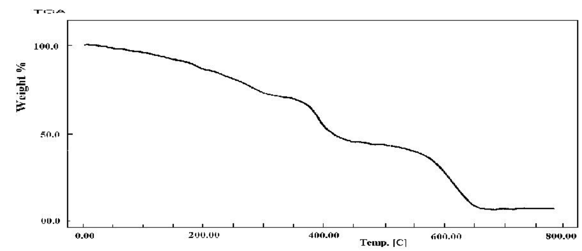


Figure 4: TGA Thermogram of modified Polyacrylamide

1.1 Metal uptake for various polymers:

The complexing behavior of the polymers was investigated on three different metal ions Fe (III), Cd (II). Adsorption of metal ions from aqueous solutions was investigated in batch experiments. The polymer was added to the metal solution of known concentration (6 ppm). The concentration of the metal ions in the aqueous phase, after the desired treatment periods (20, 40, 60, 80, and 100 min) was measured by using an atomic absorption spectrophotometer at suitable wavelength. The instrument response was periodically checked with known metal solution standards. The experiments were performed in replicates with changing the pH value (adjusted with HNO3 – NaOH). As discussed in details by several researchers **(Denizil et al., 1996; Denizil et al., 1997; Denizil et al., 2000)**, the heavy metal ions complexation behavior is more sensitive to pH changes. The low or inhibition of metal chelation with a decrease in pH was attributed to the competition of both of metal ions and protons and metal ions towards the same binding sites. On the other hand, it was reported that, the adsorption capacities increased with increasing pH. It was also reported that, "the high adsorption at higher pH values implies that metal ions interact with amino (unprotonated) groups by chelating" (**Denizil et al., 2000**).

It was found in general, that changing the pH value from the normal case 1.5 to higher value 7, has increased the adsorption rates of the metals, so, higher metals uptake were gained. The high difference between the adsorption rate in the two pH values 1.5 and 7 showed the importance of the pH value to increase or decrease the adsorption rate of the metal by the polymer. But changing the pH value to higher value 7, leads either to decrease the adsorption rates of the metals towards the polymers, or to precipitate the metal in the solution in some cases. Higher pH values than 7 leads to precipitate the metal in the solution. In some cases, the adsorption rates of the metals by the polymers were not affected by changing the pH value.

The adsorption rates of Fe (III) by polymers 1, and 2 as a function of time of the concerned pH value are plotted as shown in figure 5, and 6, respectively. The initial slopes of these curves reflect the adsorption rates. In the most cases, results showed a high adsorption rates at the beginning of measurements followed by adsorption equilibrium, which is gradually reached within 100 min (**Sağlam et al, 2001**).

Fe+3 uptakes by both polymers were clearly affected by changing the pH value. At pH 1.5 less metal was adsorbed by both of polymer 1 and polymer 2, whereas at pH 7 more metal was adsorbed from the solution. On the other hand, it was noticed that higher pH value leads to precipitate the metal in the solution. Thus, the order of Fe+3 uptakes by polymer 1 according to pH value is as follows:

Fe+3 uptake at pH 7 > Fe+3 uptake at pH 2.5 > Fe+3 uptake at pH 1.5

On the other hand data depicted from both figures shows that, modified polymer has a higher uptake value for Fe metal ions compared to unmodified one.

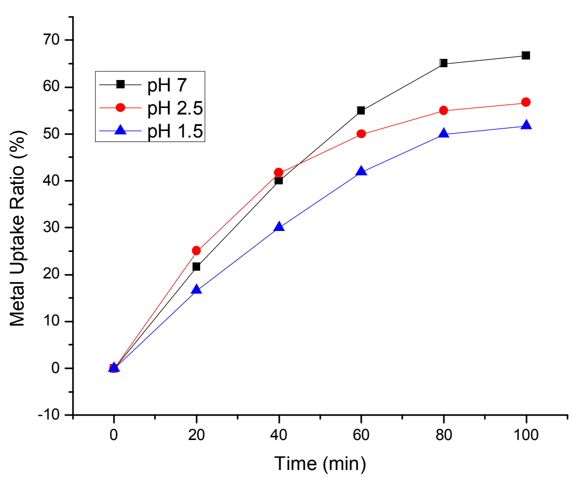


Figure 5: Effect of the pH value on the amount of Fe metal uptaked by P 2

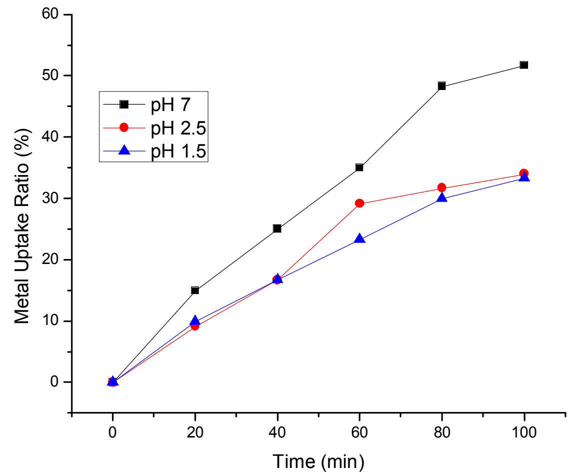


Figure 6: Effect of the pH value on the amount of Fe metal uptaked by P 1

The adsorption rates of Cd (II) by the polymers as a function of time at the concerned pH value are plotted as shown in figure 7, and 8. The initial slopes of these curves reflect the adsorption rates. In the most cases, results showed a high adsorption rates at the beginning of measurements followed by adsorption equilibrium, which is gradually reached within 100 min. Also there are different selectivities of Cd (II) towards the different polymers **(Sağlam et al, 2001).**

Cadmium (II) adsorption studies at pH 2.5, 1.5, and 7, respectively, with various polymers are discussed below:

As shown in figures 7, and 8, Cd+2 uptakes by polymer 1 and polymer 2 were clearly affected by changing the pH value. By changing the pH value from 1.5 to 2.5, the adsorption rates increased to give better results of adsorption. However, changing the pH value to 7 leads to precipitate the metal in the solution. Thus, the order of Cd+2 uptakes by both polymers according to pH value is as follows:

Cd+2 uptake at pH 1.5 > Cd+2 uptake at pH 2.5

On the other hand data depicted from both figures shows that, modified polymer has a higher uptake value for Cd metal ions compared to unmodified one.

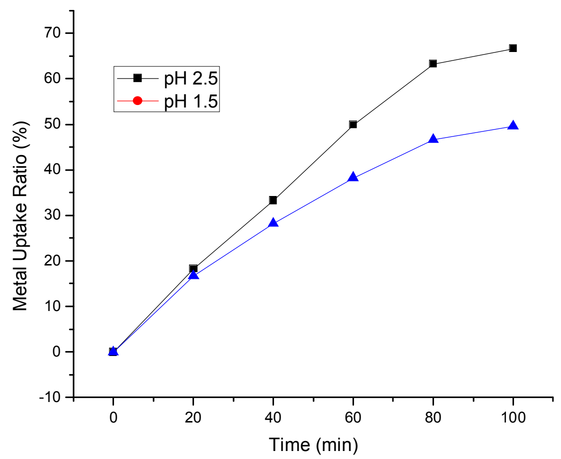


Figure 7: Effect of the pH value on the amount of Cd metal uptaked by p2

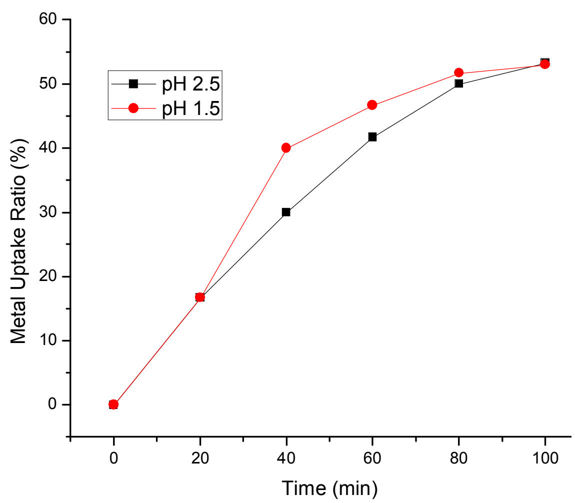


Figure 8: Effect of the pH value on the amount of Cd metal uptaked by p1

4. Conclusion

In this study amino groups has been introduced to polyacrylamide polymer chains by grafting with ethylene diamine compound. The produced modified polymer has been characterized with different techniques such as elemental analysis, TGA, and IR techniques to show the differences before and after grafting. The modified polymer showed a higher tendency to remove heavy metals in particular to have a complexion behavior with Fe (III), and Cd (II) metal ions.

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