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Adsorption of Heavy Metals in Seawater Using Amidoxime Fibers Prepared by Gamma Irradiation Technique

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Abstract

For safety and safeguards purposes, amidoxime fibers were investigated for the ability to adsorb heavy metals from seawater. Amidoxime fibers were successfully synthesized by the simultaneous irradiation grafting technique at low temperature using Co-60 as the gamma ray source. The degree of cografting of AN/MAA onto LDPE fibers at the total dose of 40 kGy was calculated to be approximately 52%. The fibers exhibit the ability to adsorb Pb and As form seawater. Under the studied conditions, for the case of Pb, the adsorption capability was 5.33 – 33.50 g-Pb/kg-adsorbent. For the case of As, the adsorption capability was approximately 0.25 – 0.77 g-As/kg-adsorbent. The adsorption also reduced with submerging time. Thus, the amidoxime fibers can be used as a very effective detector for Pb and As in seawater for the submerging time as short as 1 week.

Keywords: Amidoxime, Heavy metals, Gamma irradiation

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Introduction

Throughout history and in the present time, chemical and biological weapons have been used to cause harmful and sometimes fatal effects to people. One of such cases was the terrorist attack in Tokyo on March 20,1995, where the sarin nerve gas was released in the Tokyo subway, killing 13 people and some 5,500 others were injured to varying degrees. In the First World War, arsenic was applied in chemical weapons. In the Vietnam War, dimethyl arsenic acid was applied for the destruction of rice cultures.

Protective measures can be taken in situations with related threat from CBRN weapons. There is an institution established for management of this problem, which is Chemical, Biological, Radiological and Nuclear Centres of Excellence (CBRN CoE) for the mitigation of and preparedness against risks related to CBRN materials and agents. The origin of these risks can be criminal (proliferation, theft, sabotage and illicit trafficking), accidental (industrial catastrophes, in particular chemical or nuclear, waste treatment and transport) or natural (mainly pandemics but also the consequence of natural hazards on CBRN materials and facilities). The CBRN CoE Initiative seeks to boost cooperation at national, regional and international levels, and to develop a common and coherent CBRN risk mitigation policy at national and regional level. Risk mitigation comprises prevention, preparedness and post-crisis management.

With the rapid development of global industry and the advent of new technologies, environmental contamination has presented a great threat to human health, especially the amounts of heavy metal ions in wastewater.

Various methods such as chemical precipitation, oxidation, reduction, ion exchange, reverse osmosis, membrane separation, filtration, electrolysis and adsorption have been used to remove and recover toxic contaminants from industrial effluents. For example, radiation-induced grafting of cellulose has been used for adsorption of hazardous water pollutants (L. Wojnarovits. et. al., 2010) and grafting of acrylonitrile onto chitin has been used for adsorption of arsenic in water (Thong T.H. et. al., 2015).

Currently, there are a number of industrial factories which use chemicals in manufacturing processes which are located near rivers and sea. Sometimes, they intentionally release wastewater to rivers and sea. Therefore, for safety and safeguards purposes, wastewater must be continually monitored. The amidoxime chelating functional groups may have the ability to adsorb heavy metals in seawater besides uranium. Therefore, the purpose of this research work is to detect heavy metals in seawater using the amidoxime adsorbent.

Objective

To investigate amidoxime fibers prepared by gamma irradiation for the ability to detect heavy metals in seawater

Scope of research

1. Synthesize amidoxime fibers using gamma radiation
2. Collect seawater sample from the Andaman Sea at Phuket Marine Biological Center
3. Study adsorption of 2 heavy metals (Pb and As) in seawater
4. For each heavy metal, study 3 concentrations in seawater
5. Recover adsorbed heavy metals from the amidoxime fibers

Experiment and method

Preparation of amidoxime fibers

Irradiation-induced cograft polymerization

To prepare LDPE fibers for cograft polymerization, LDPE fibers were washed with deionized water (DI) and dried in a forced-convection oven at 50ºC for 24 hours to obtain a constant weight. The weight of LDPE fibers was recorded.

The fibers were immersed in a container containing two monomers with a mixing ratio of 60 : 40 [acrylonitrile (AN) : methacrylic acid (MAA)] by volume. The presence of MAA enhanced the hydrophilicity of the fibers, and this optimized mixing ratio was adopted from Kawai's work (Kawai T. et. al., 2000). The mixture of the two monomers was diluted in 50 (w/w)% DMSO as a solvent.

The simultaneous irradiation cografting method at low temperature was achieved by putting ice cubes around the container for irradiation. The container was irradiated with gamma-ray from Co-60 at 40 kGy (Vareeporn, 2014).

(a) Ice cubes around the container

(b) Gamma-ray radiator

Figure 1. Ice cubes around the container for irradiation and gamma-ray radiator

After irradiation, the fibers were removed from the container and were thoroughly washed with DMF several times to completely remove homopolymer formation. The fibers were washed with deionized water (DI) and dried in a forced-convection oven at 50ºC for 24 hours to obtain a constant weight. The weight of cografted fibers was recorded. The degree of cografting was calculated from the weight gain using the following formula:

$$\text{Degree of cografting} = \frac{(W_1 - W_0)}{W_0} \text{x} 100$$

Where W_0 is the weight of the starting fibers and W_1 is the weight of the cografted fibers. Then, the cografted fibers were investigated for the characteristic band of the cyano group by Fourier Transform Infrared (FTIR) Spectroscopy technique.

Amidoximation of cyano group

The cyano groups of the cografted fibers were converted into the amidoxime groups by immersing the cografted fibers in 3 (w/v)% NH_2OH-HCl solution at 77 ºC for 1.5 hours. The fibers were subsequently washed with 50 : 50 (v/v)% methanol : DI water and immersed in 1 M HCl solution for 15 minutes. The amidoxime fibers were washed DI and dried in a forced-convection oven at 50 ºC for 48 hours to obtain a constant weight. The weight of the amidoxime fibers was recorded. Alkaline treatment of fibers was performed by submerging in a potassium hydroxide (KOH) solution at 80 ºC for 1 hour. Then, the amidoxime fibers were repeatedly washed with DI water until pH of 9 of the rinse was obtained. Finally, the fibers were dried in a forced-convection oven at 50ºC for 48 hours to obtain a constant weight. The weight of the amidoxime fibers was recorded and the amidoxime group density was calculated from the weight gain using the following formula:

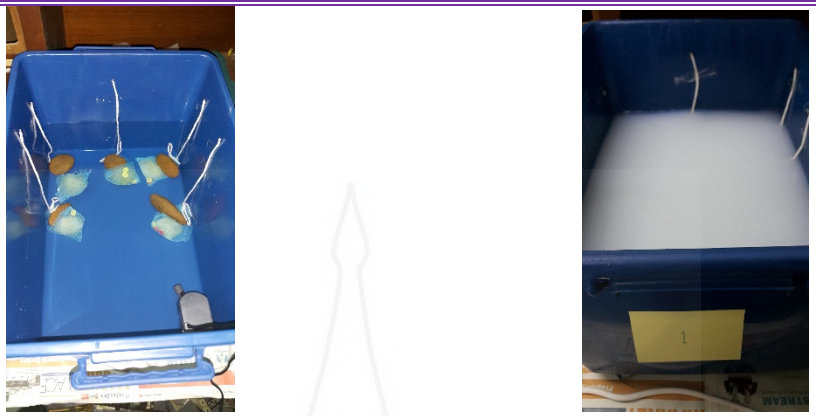
$$\text{Amidoxime group density (mol/kg)} = \frac{(W_2 - W_1)}{69.5W_2} \text{x1000}$$

Where W_2 is the weight of the amidoxime fibers and the number 69.5 represents the molecular weight of hydroxylamine hydrochloride, NH_2OH-HCl (Saito K. et. al., 1987). Then, the amidoxime fibers were investigated for the characteristic bands of the amidoxime group using the FTIR technique. The amidoxime fibers were placed in bags constructed of loosely-woven plastic fibers. The lose surfaces of the plastic bags ensured no obstruction to the flow of seawater.

Figure 2. Plastic bag containing amidoxime fibers

To test heavy metal adsorption efficiencies of amidoxime fibers, the fibers in the plastic bags were submerged in a sample of seawater in a 50-L plastic container in a laboratory at room temperature. The seawater sample was collected from Phuket Province, Thailand. For the study of Pb adsorption, 3 concentrations in seawater were studied: 0.2, 1 and 2 g/L (concentration 1, 2 and 3, respectively, in Table 1). For the study of As adsorption, 3 concentrations in seawater were studied: 0.25, 0.625 and 1.25 g/L (concentration 1, 2 and 3, respectively, in Table 1). The submerging time was 1, 2, 3 and 4 weeks.

The reason for choosing these concentrations is because during a postulated accident, released quantities of Pb and As are assumed to be much higher than the regulatory limit for discharge into water. Thus, the concentrations of 1,000, 5,000 and 10,000 times of the regulatory limit for lead and 1,000, 2,500 and 5,000 times for arsenic were chosen.



(a) System before addition of heavy metals (b) System after addition of heavy metals

Figure 3. 50-L plastic container for the study

Amidoxime fibers were removed from the seawater sample, washed with DI water and dried in a forced-convection oven at 50°C for 1 hour. They were then immersed in 1 M HCl at 50 °C for 1 hour in order to elude adsorbed metals. The HCl solution with eluents was dried and added with 30 mL 1% nitric acid solution to prepare for an analysis by inductively coupled plasma mass spectrometry (ICP-MS).

Results and discussion

1. Degree of cografting

The degree of cografting of AN/MAA onto LDPE fibers at the total dose of 40 kGy was calculated to be approximately 52%. This value was lower than that of the recent study, which obtained approximately 78%. This was because this other study treated LDPE fibers with chromic acid before irradiation grafting in order to increase the surface area of the substrate (Vareeporn, 2014).

2. Amidoxime group density

The amidoxime group density was calculated to be approximately 2.49 mol/kg.

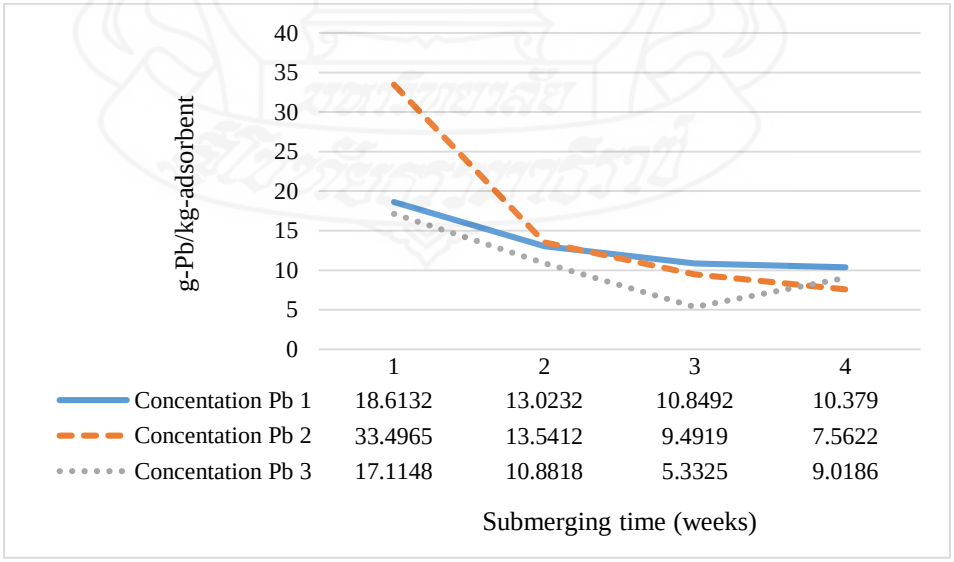
3. Heavy metals adsorption efficiency amidoxime fibers

Results from ICP-MS analysis are shown Table 1 and plotted in Figure 4. in order to show the trends. For concentration 1, the adsorption efficiencies for Pb for the submerging time of 1, 2, 3 and 4 weeks were 18.6132, 13.0232, 10.8492 and 10.3790 g-Pb/kg-adsorbent, respectively. For As, they were 0.5938, 0.5708, 0.3842 and 0.3970 g-As/kg-adsorbent, respectively. For concentration 2, the adsorption efficiencies for Pb were 33.4965, 13.5412, 9.4919 and 7.5622 g-Pb/kg-adsorbent, respectively. For As, they were 0.7704, 0.4647, 0.3094 and 0.3147 g-As/kg-adsorbent, respectively. For concentration 3, the adsorption efficiencies for Pb was 17.1148, 10.8818, 5.3325 and 9.0186 g-Pb/kg-adsorbent, respectively. For As, they were 0.5107, 0.4706, 0.2484 and 0.2780 g-As/kg-adsorbent, respectively. The adsorption efficiency for Pb was substantially higher than that of As. Moreover, the adsorption reduced with submerging time and did not appear to be significantly affected by the concentrations of heavy metals in seawater under the studied conditions.

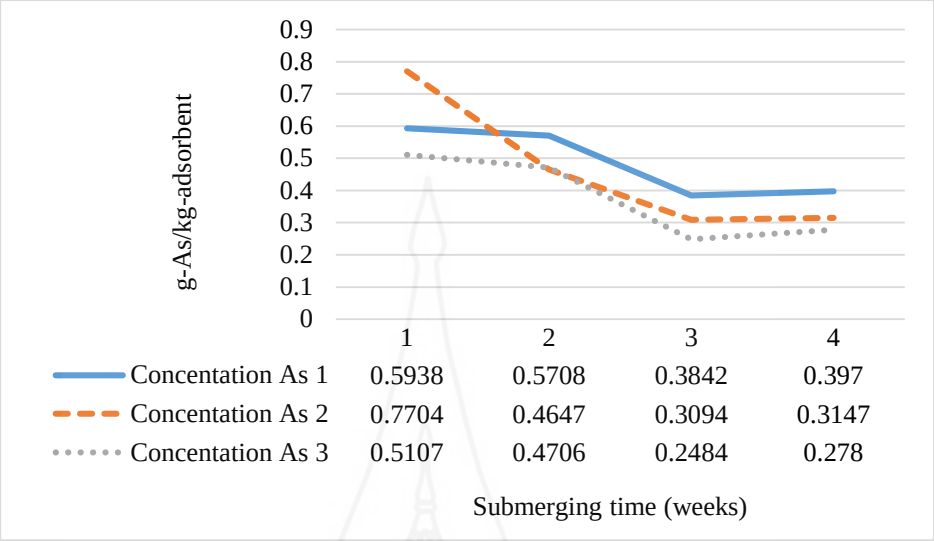
The adsorption efficiencies for both Pb and As for concentration 3 were lower than those of concentration 2. This is because more suspended particles were formed with increasing Pb and As concentration. Those particles physically prevented amidoxime functional groups from absorbing Pb and As ions, resulting in lower adsorption with increasing heavy metal concentrations.

Table 1. Results of heavy metals adsorption of the amidoxime fibers

Concentration of heavy metal	Submersion duration (weeks)	Elements	
		Pb (g-Pb/kg-adsorbent)	As (g-As/kg-adsorbent)
1	1	18.6132	0.5938
	2	13.0232	0.5708
	3	10.8492	0.3842
	4	10.3790	0.3970
2	1	33.4965	0.7704
	2	13.5412	0.4647
	3	9.4919	0.3094
	4	7.5622	0.3147
3	1	17.1148	0.5107
	2	10.8818	0.4706
	3	5.3325	0.2484
	4	9.0186	0.2780



(a) Adsorption of Pb



(b) Adsorption of As

Figure 4. Results of heavy metals adsorption of the amidoxime fibers (Results from Table 1)

4. FTIR analysis of functional groups

Characteristic absorption bands of functional groups were investigated by the FTIR technique. For the FTIR spectra of the LDPE fiber shown in Figure 5, the characteristic absorption bands of polyethylene at wave numbers 2849 and 1463 cm^{-1} due to C-H alkyl stretch and C-H, respectively, are clearly present. In fact, as expected, these two absorption bands are present in all spectra. The characteristic absorption bands of cografted AN/MAA appear at wave numbers 2243 and 1712 cm^{-1} due to C≡N of poly(acrylonitrile) and C=O of poly(methacrylic acid), respectively, as shown in Figure 6. After the amidoxime group conversion, the C≡N band at wave number 2243 cm^{-1} disappears, and the N-H stretch band of the amidoxime group at wave number 3360 cm^{-1} as well as the C=O band of the amidoxime group at wave number 1657 cm^{-1} become present, as shown in Figure 7.

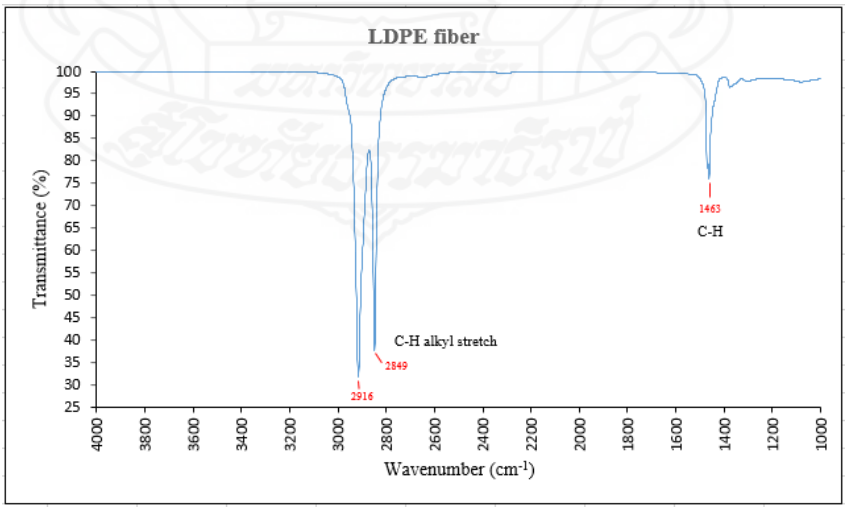


Figure 5. FTIR spectra of LDPE fiber

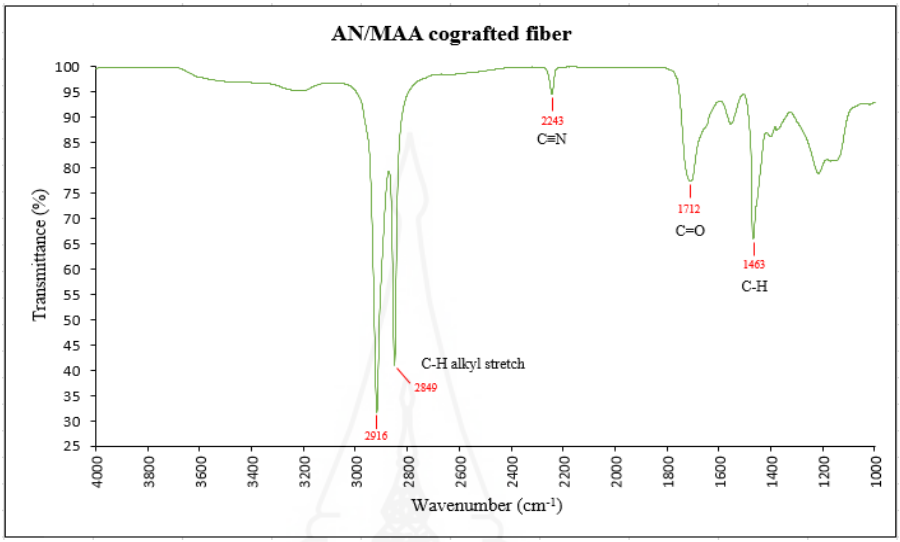


Figure 6. FTIR spectra of AN/MAA cografted fiber

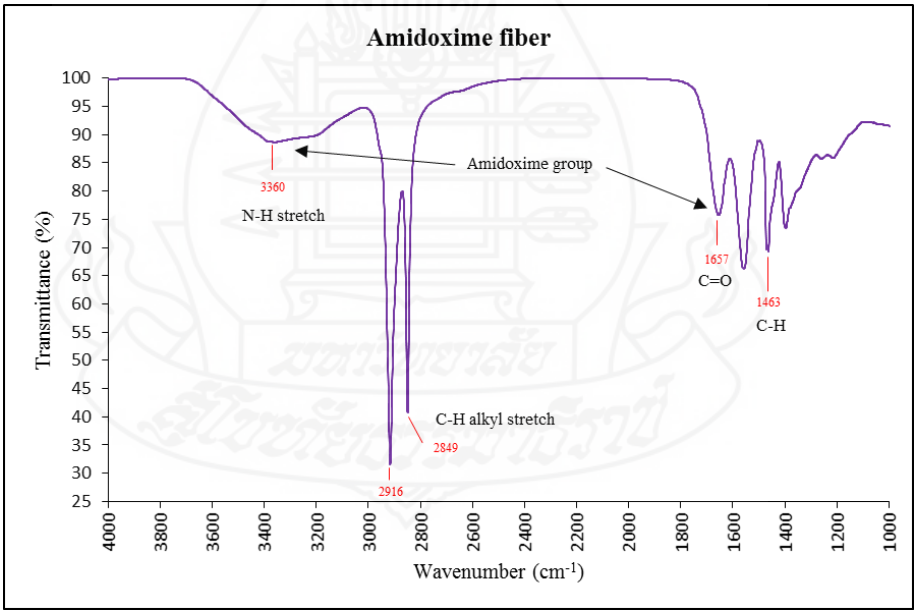


Figure 7. FTIR spectra of amidoxime fiber

Conclusions

Amidoxime fibers were successfully synthesized by the simultaneous irradiation grafting technique at low temperature using Co-60 as the gamma ray source. The degree of cografting of AN/MAA onto LDPE fibers at the total dose of 40 kGy was calculated to be approximately 52%. The fibers exhibit the ability to adsorb Pb and As form seawater. Under the studied conditions, for the case of Pb, the adsorption capability was 5.33 – 33.50 g-Pb/kg-adsorbent. For the case of As, the adsorption capability was approximately 0.25 – 0.77 g-As/kg-adsorbent. The adsorption also reduced with submerging time. Thus, the amidoxime fibers can be used as a very effective detector for Pb and As in seawater for the submerging time as short as 1 week.

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