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Araştırma Makalesi / Research Article

Removal of Heavy Metal Ions with Phenoxy Substituted Cyclotriphosphazene Derivatives Bearing Imine

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Abstract

Keywords
Phosphazene;
Cyclotriphosphazenes;
Organophosphazene;
Imine;
Adsorpsion.

Hexa [4-(4-hydroxy-phenyliminomethyl) phenoxy] cyclotriphosphazene (**A1**) and Hexa [4-(2- hydroxy-phenyliminomethyl) phenoxy] cyclotriphosphazene (**A2**) were derived from the reactions of hexa(4-formyl-phenoxy)cyclotriphosphazene and hexa(2-formyl-phenoxy)cyclotriphosphazene with 4-aminophenol and 2-aminophenol. Adsorption process in an aqueous solution of Cu, Fe, Mn and Zn ions of the organophosphazenes bearing imine groups were performed depending on the initial concentration of metal ions and time. All of the compounds adsorbed the selected metal ions in the first 10 minutes. When the initial concentration of metal ions increases, the amount of metal ions adsorbed of organophosphazene with imine groups increased. Although the chemical structures of the compounds are different, the amount of adsorbed metal was about the same.

İmin Grupları Taşıyan Fenoksi Sübstitüe Siklotrifosfazen Türevleri ile Ağır Metal İyonları Giderimi

Öz

Anahtar kelimeler
Fosfazan;
Siklotrifosfazen;
Organophosphazene;
İmin; Adsorpsion.

Hekza[4-{(4-hidroksi-fenilimino)metil}fenoksi]siklotrifosfazenin(**A1**) ve hekza[4-{(2-hidroksi-fenilimino)metil}fenoksi]siklotrifosfazenin(**A2**), 4-aminofenol ve 2-aminofenol ile heksa (4-formil-fenoksi) siklotriposfazen ve heksa (2-formil-fenoksi) siklotriposfazen reaksiyonlarından türetildi. İmin gruplarını taşıyan organofosfazelerin sulu Cu, Fe, Mn ve Zn iyonları çözeltisinde adsorpsiyon işlemi, metal iyonlarının başlangıç konsantrasyonuna ve süresine bağlı olarak gerçekleştirildi. Bileşiklerin tümü seçilen metal iyonlarını ilk 10 dakika içerisinde adsorbe etti. Metal iyonlarının başlangıç konsantrasyonu arttığında, imin gruplarıyla organofosfazene adsorbe edilen metal iyonlarının miktarı arttı. Bileşiklerin kimyasal yapıları farklı olmasına rağmen, adsorbe edilen metal miktarı yaklaşık olarak aynıydı.

1. Introduce

Phosphazenes are involved in inorganic and organic chemistry. Phosphazenes are compounds of the structure R3P=N-R (R, halogen, alkoxy, amino, alkyl and aryl) of the same group (VA) nitrogen and phosphorus atoms (Allcock, 1972). There are three different groups of phosphazene compounds, linear (1), ring (2) and poly (3). (Figure 1.). In the linear phosphazenes, three side groups are bound to three phosphorus atoms, while in the ring and poly phosphazenes, two side groups are bound to each phosphorus atom. These side groups can be halogens, a wide variety of organic or organometallic compounds (Allen, 1994).

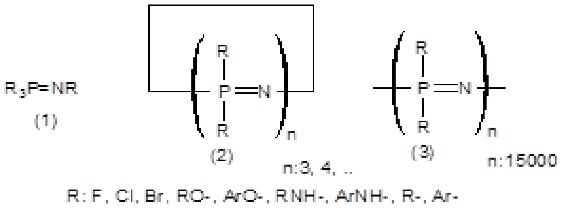

Figure 1. Structure of phosphazene compound groups.

Organophosphazenes are synthesized from the reactions of halophosphazenes and organic nucleophiles. It is estimated that over 10,000 different ring and linear organophosphazenes have been synthesized to date. Among these organophosphazenes, the number of organophosphazenes that carry groups such as formyl, imine and oxime is quite low. New organophosphazene derivatives of formyl and imine, which are our study subjects, were performed at room temperature and room atmosphere.

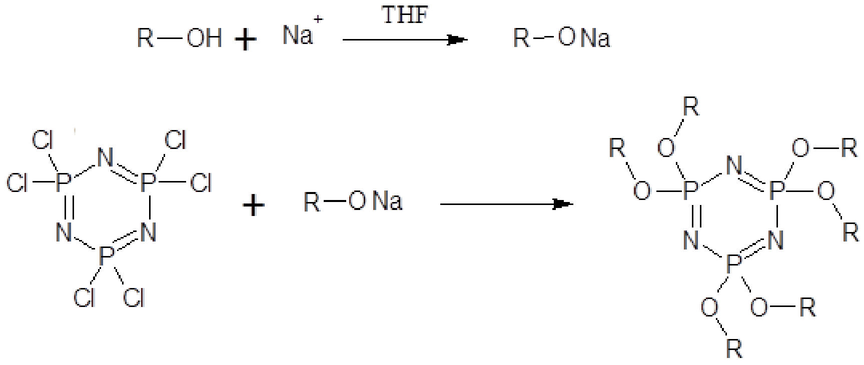

Figure 2. Reaction of halophosphazene with sodium phenolates

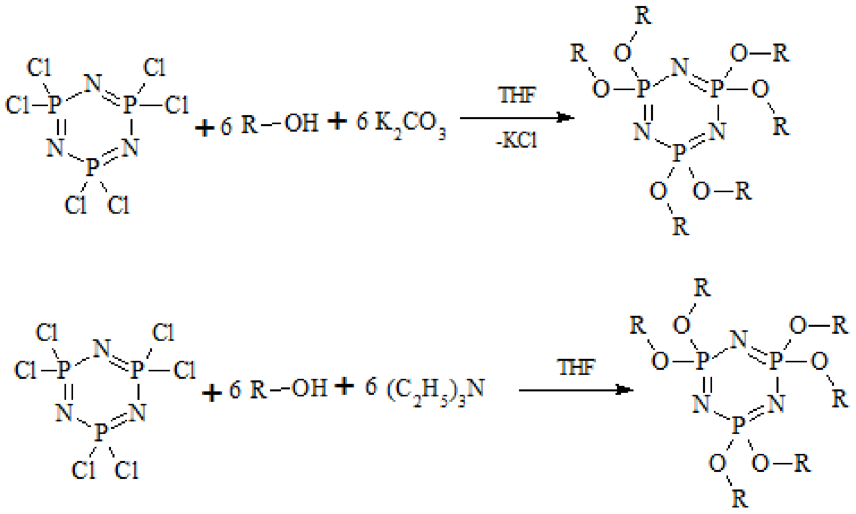

Figure 3. Synthesis of organophosphazen from the reaction of halophosphazen with phenol in the presence of base

1.1 Reaction Mechanism of Halophosphazenes with Phenols

The reaction of halophosphazenes and phenols is carried out in one of two methods. In the first method, the salt of the phenol with metallic sodium is first prepared and then reacted with halophosphazene. This reaction results in organophosphazene and NaCl. The phenolate acts as nucleophilic in the displacement.

In the second method, the reaction of halo phosphazene with phenol takes place in the presence of one of the bases such as carbonates of group 1A or triethylamine. The base used is said to serve to retain the HCl formed in the reaction. This method is simpler than the first method. Because in the first method must to prepare the salt of phenol. Since the phenol salts have the ability to decompose by air, the reaction should be carried out in an airless environment.

1.2 Reactions of Halo Phosphazenes with Formyl-bearing Phenols

Formyl-bearing organophosphazenes are derived from the reactions of hexa chloro cyclo triphosphazene with 4- hydroxybenzaldehyde, 2-

hydroxybenzaldehyde, sodium 4- formyl - 3- methoxyphenate, 4 - hydroxyl - 3 - methoxybenzaldehyde, 2 - hydroxyl – 4 - methoxybenzaldehyde, 5 - bromo - 2 - formylbenzaldehyde and 5- chloro - 2- formylbenzaldehyde. Both methods were used in these studies. All of the studies were carried out in airless environment Both methods were used in these studies. But second method was more used. All of these reactions were carried out in an airless environment.

Carriedo et al. (1996) obtained hexa (4-formyl-phenoxy) cyclotrifosphazene in the THF solvent of 4-hydroxybenzaldehyde and in the presence of K_2CO_3 in the presence of 91% of the hot reaction with hexa-chlorobenzoyl triphosphazene (Figure 4). In this reaction, 6 moles of 4-hydroxybenzaldehyde N3P3Cl6, 14.4 moles of K_2CO_3 $N_3P_3Cl_6$ were used (Cariedo et al., 1996). They obtained the same compound at room temperature and 92% yield, using 6.07 moles of 4-hydroxybenzaldehyde $N_3P_3Cl_6$ and 12.16 moles of K_2CO_3 $N_3P_3Cl_6$ (Cil et al., 2006). In both studies, the reaction was continued for 48 hours in the absence of air.

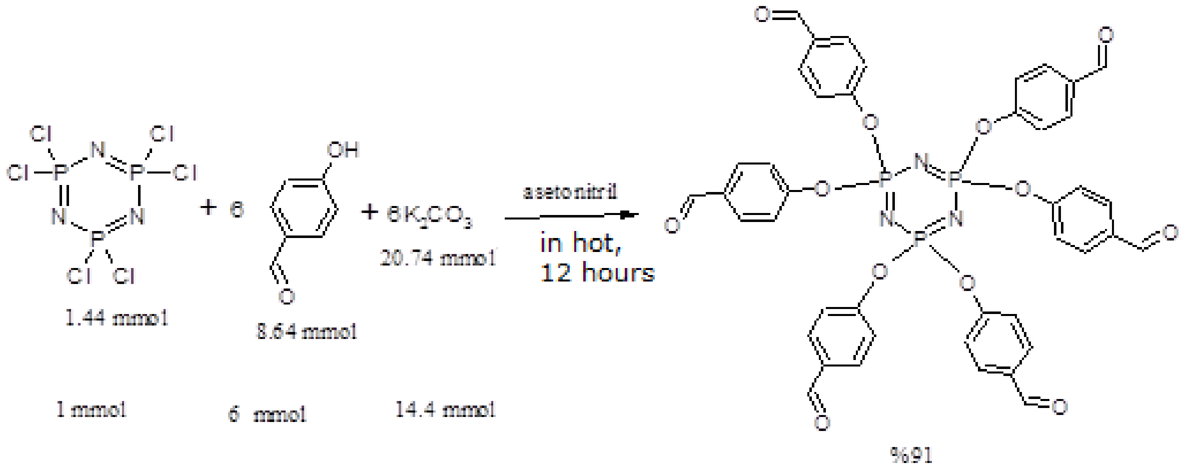

Figure 4 Synthesis reaction of hexa (4-formyl-phenoxy) cyclotrifosphase.

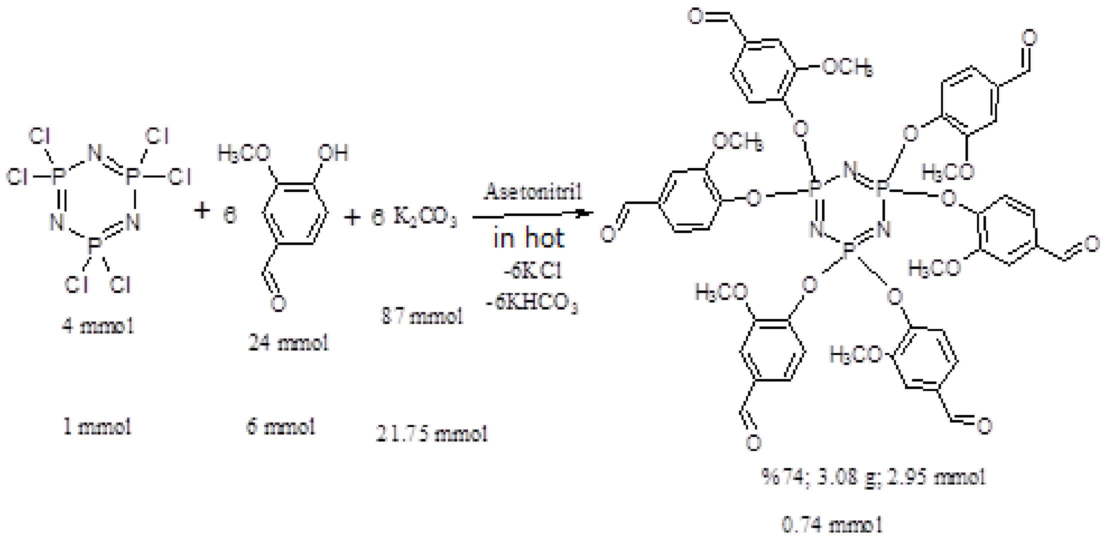

Figure 5. Synthesis of hexa (4-formyl-2-methoxyphenoxy) cyclotriphosphazene.

Tümer et al (2008) in the presence of K_2CO_3 in the acetonitrile solvent of 4-hydroxy-3-methoxybenzaldehyde with hexachlorocyclotrifosphazene, they obtained hexa (4-formyl-2-methoxyphenoxy) cyclotrifosphazene in a 74% yield from in the hot reaction at 48 hours (Tumer et al., 2008). In this reaction, 6 moles of 4-hydroxy-3-methoxybenzaldehyde $N_3P_3Cl_6$, 21.75

moles of K_2CO_3 $N_3P_3Cl_6$ were used. The reaction was carried out in airless medium (Figure 5).

Yuan et al (2005) obtained hexa (4-formyl-phenoxy) cyclotrifosphazen compound in 88% yield from the reaction of hexaklorosiklotrifosfazene with sodium 4-formylphenolol in THF at 48 hours in hot (Yuan et al., 2005). This reaction was carried out in the airless medium (Figure 6).

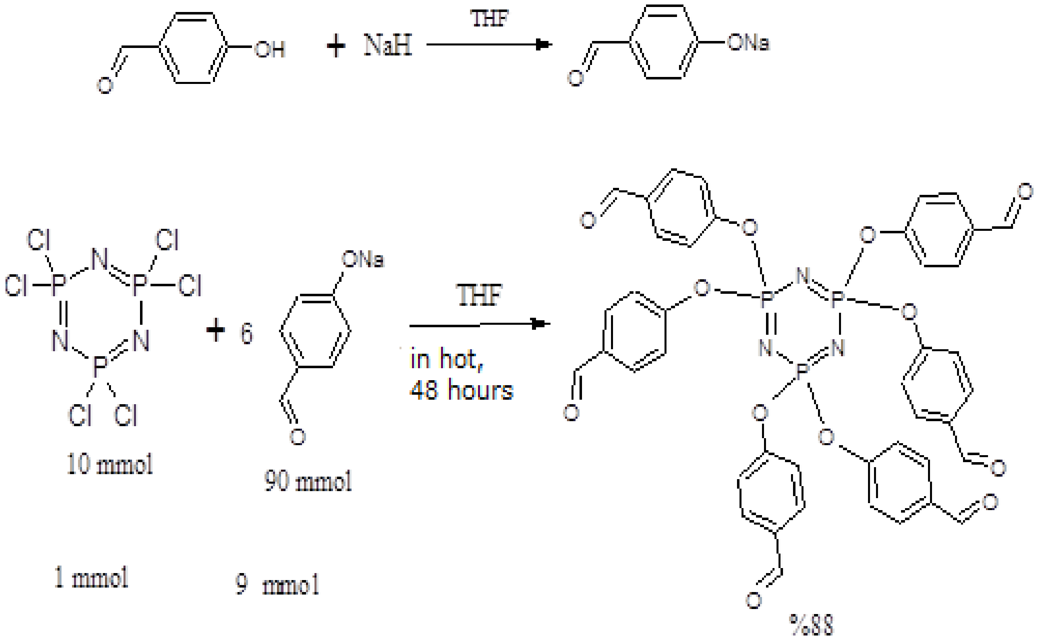

Figure 6. Synthesis of hexa (4-formyl-phenoxy) cyclotriphosphazene from sodium 4-formyl-phenol.

1.3 Immin Bearing Organophosphazenes

The imines are derived from the acid-catalyzed reaction of amines with aldehydes and ketones. Such compounds were first introduced by Schiff, It is also called Schiff base. Imine compounds derived from aromatic aldehyde and aromatic amines are more stable.

Few studies have been done on the synthesis of imine-bearing organophosphazenes from the reactions of formyl-bearing organophosphazen with primary amines. In studies, hexa (4-forylphenoxy) cyclotrifosphazen, hexa (2-formyl-phenoxy) cyclotrifosphazen, hexa (4-bromo-2-formyl-phenoxy) cyclotrifosphazen, hexa (4-chloro-2-formyl-phenoxy) cyclotrifosphazen, hexa (4-amino-3-methyl-phenoxy) cyclotrifosphazen, 1- {2- [1,3-di (oxytetrathehlenoxy) -3,5,5-tri (2-formyl-phenyloxy) cyclotrifosphazen] oxyethylamino} antraquinone and 1,3-oxytetraethyloxy) -1,3,5,5-tetra (2-formyl-phenoxy) cyclotrifosphazen as formyl bearing organophosphazen used (Aslan et al., 2008, Ozturk et al., 2013).

1.4 Adsorption and Adsorption Types

The adherence of atoms, ions or molecules on a solid surface is called adsorption. The separation of the suspended particles from the surface is called desorption. The rate and amount of adsorption is a function of the adsorbing surface. For this, substances which surface area according to the mass is larger, preferred. If the pressure increases during the adsorption of gases, the adsorbent may adsorb more of the substance. The same applies to adsorption of solutions. Adsorption of the solution; temperature depends on the nature of the substance to be adsorbed and the concentration in the solution (Karaman, 2010).

The adsorption of gases and liquids (in solution) has three successive velocity steps. The first is the transport of adsorbed material to the outer surface of the adsorbent as a film (film diffusion), the second is the diffusion within the adsorptive pores (Pore diffusion). In the last step, adsorption of adsorbent material onto the adsorbing pore surface occurs. Usually the last step is very fast. In the adsorption of liquids, adsorption is caused by the interest of the solid matter against the solute. This surface phenomenon is due to the electrical attraction of the solvent applied to the adsorbent, the Van der Waals forces or the chemical structure.

1.5 Adsorption Types

There are three different types of adsorption depending on the type of attraction forces between adsorbed molecules and adsorbing surface.

1. Physical adsorption: Physical adsorption occurs as a result of physical attraction forces between the solid surface and the adsorbed substance molecules. Physical adsorption; the forces that bind adsorbed molecules to the adsorbing surface are weak Van der Waals forces. Desorption is easier and faster because the attraction forces are weak. Physical adsorption is generally observed at low temperature. It is characterized by low energy adsorption. Physical adsorption is reversible, and the process is very fast. As the temperature increases, physical adsorption is generally reduced (Berkem and Baykut, 1984).

2. Chemical adsorption: Chemical adsorption is caused by the chemical bond between adsorbing molecules and adsorbing surface molecules or atoms. This type of adsorption in the chemical interaction is more difficult for desorption. Chemically adsorbed molecules cannot move freely at the interface. The bond which between the absorbing and adsorbed, is strengthened by the increase in temperature as in chemical reactions.

3. Ionic adsorption: The effect of electrostatic gravitational forces between adsorbed and adsorbent is the attachment of ions on the surface. It is important that the adsorbing and adsorbed materials have opposite electric charges and that the surfaces attract each other. Electric charge and small diameter ions are better adsorbed.

It is difficult to explain the adsorption process by one of the types of adsorption outlined above. In many cases, physical and chemical activation happens together. Some substances are physically absorbable at low temperatures and chemically at high temperatures. In the case of many adsorptions, different types of adsorption can be seen together or in succession (Berkem and Baykut, 1984).

1.6 Parameters Affecting Adsorption

Some of the important parameters affecting the adsorption process are summarized below (Karaman, 2010, Savcı, 2010).

Surface area: Adsorption is a surface event. It is therefore proportional to the specific surface area. The specific surface area is defined as the part of the total surface area suitable for adsorption. The size of the particle size of the adsorbent is small, the surface area is large and porous, and generally increases the adsorption. In addition, functional groups on the surface are also important factors affecting the adsorption behavior of the adsorbent.

Type and properties of adsorbing and adsorb material: Solubility of the solute in liquids is a controlling factor for the balance of adsorption. In general, there is an inverse relationship between the rate of adsorption of the solute and its solubility in the liquid phase. A water-soluble (hydrophilic) substance is less adsorbed than water-soluble (hydrophobic) material. Molecular size also affects adsorption. The molecule of the size most suitable for the pore size of the adsorbent is adsorbed better.

pH value of the medium: pH value of the solution in the event of adsorption is an important control parameter. Due to the strong adsorption of H + and OH- ions, the adsorption of other ions is affected by the pH of the solution. In general, the adsorption rate increases at pH where the substances are neutral. If there is too many hydrogen or hydroxyl ions in the environment, these ions enter the surface with the adsorption substance ions. This may result in less surface coating with adsorbed substance molecules, ie less adsorption.

Temperature: Adsorption reactions are generally exothermic, ie heat transfer reactions. Therefore, adsorption is generally increased as the temperature decreases. However, if the reaction is endothermic, ie, it is a reaction that takes heat from the environment, the adsorption will increase with increasing temperature. Small changes in temperature do not significantly affect the adsorption process.

1.7 Adsorbent Types and Properties

For the use of an adsorbent in industrial processes; It should be easy to find, be cheap, be reusable, do not enter into chemical reactions, have a large surface area per unit mass, adsorption capacity of adsorption to the desired liquids and gases, high selectivity against the substance to be required to show.

Various chemicals are used for adsorption techniques in water treatment. Silica gel, füller soil, pore size large resins, ion modifier resins with large pore sizes, active silica and activated carbon are the most well-known adsorbents.

Silica gel is a granular and porous form of silicon dioxide synthetically produced from sodium silicate, water and glass content. It is used in dehydration of air and other gases, fractionation of hydrocarbons.

Molecular sieves; porous, synthetic zeolite crystals are silver alumina silicates. They are uniform porous and different from other adsorbents. Different zeolites have 3-10 Å pore size.

Fuller soil (magnesium aluminum silicate); petroleum fractions, vegetable and animal oils are used in the purification. A porous structure is formed by heating and drying the clay.

Activated clays; bentonite and other clays. They do not have adsorptive properties when they are not activated with acid (H_2SO_4 or HCl). After activation with H_2SO_4 or HCl, the mixture is washed and dried. It is used in particular color removal of petroleum products by gaining a fine powdered structure.

Molecular activated carbon; custom made. 5 - 5.5 Å (Å = 10-10 m) open pore structure. These pores can pass paraffin hydrocarbons but do not undergo large molecular diameter isoparaffins. Acetylene components are used to separate alcohols, organic acids, ketones, aldehydes. Synthetic polymeric adsorbents (resins); They are porous spherical particles with a diameter of 0.5 mm. Each particle is formed by a combination of microspheres of 10-4 mm diameter.

Bauxite (hydrated Al_2O_3); It is used in the filtration of oil fractions, especially in the dehydration of gases. The adsorption capacity is increased by increasing the temperature from 230 0C to 815 0C in the naturally occurring form of the hydrated alumina. It is also used in color removal of petroleum products and drying gases.

Alumina; has a hard structure. Activated hydrated aluminum oxide is formed which by removed heating the moisture in its structure. The porous product is used in granular or powder form.

Bone charcoal; It is obtained from dried coal at 600 - 900 °C. It is used for the purification of sugar, to remove the ash from the solutions. Color relieving; It is used in the purification, purification of organic or inorganic substances, purification of sugar, vegetable and animal oils.

Gas adsorbent carbon; It is obtained by carbonization of coconut shells, fruit peels, coal, lignite and wood. It must be activated by hot oxidation with hot air or alum. It is used in granule or pellet form. The recovery of solvent vapors from gas mixtures is used to remove industrial odors, CO_2 and other industrial gases, gas masks and fractionation of hydrocarbons.

Zeolites are used in drying, separation of hydrocarbons and in many applications. Activated carbon; It is a microcrystalline material obtained by thermal decomposition of wood, fruit shells and coal. The average pore diameter, 10-60 Å surface area is 300 - 1200 m2 / g. It is used in the adsorption of organic substances.

Organophosphazenes were synthesized by nucleophilic displacement reactions (SN1 or SN2) with organic groups because the phosphorous halogen linkage of halophosphazenes in which the halos (F, Cl, Br) are active in the side group. The reactions of phosphazenes with organic groups such as alcohols, phenols, amines (primary or secondary), thiols, organometallics, carboxylic acids and amides have been investigated. The most studied organic groups are alcohols, phenols and amines. The desired substituted phosphazene compounds could not be obtained in the reaction with carboxylic acids and amides.

Those polyphosphazenes; There are a wide range of applications such as medicine, microlithography, construction of materials that delay or prevent burning. Because polyphosphazenes; solid fibers, films, glasses and elastomers commonly used in the state-of-the-art technology, can serve as solid electrodes and electronic conductors, as carriers of immobilization of macromolecular biomedical agents, chemotherapeutic agents, enzymes or transition metal catalysts. Wide application areas lead to a focus on polyphosphonases (Allcock, 1987).

In this study, the adsorption of **A1** and **A2** compounds derived from hexa (4-formyl-phenoxy) cyclotrifosphazen and hexa (2-formylphenoxy) cyclotrifosphazen and 4-aminophenol and 2-aminophenol in some heavy metal-containing aqueous solutions were investigated. The results of the analysis revealed that imine - bearing organophosphazenes adsorb heavy metals. The heavy metal (Cu, Fe, Mn and Zn) adsorption property of these newly synthesized compounds was made for the first time with this study. These atoms were preferred because heavy metals such as copper, iron, manganese, zinc play very important roles in cell functions.

2. Material and Method

2.1 Used Solvents and Chemical Substances

THF, acetonitrile, ethyl alcohol, dichloromethane, acetone and diethyl ether solvents were used in the synthesis and purification of the compounds. All reactions were carried out at ambient temperature and ambient atmosphere.

A1 and **A2** compounds were synthesized by the method described in the literature (Aslan et al., 2010, Aslan et al., 2017). The structure of the compounds is given in Figure 7. The characteristic data, IR and NMR of the compounds were given by Aslan et al.(2017) Data of the compounds **A1** and **A2** were given in Table 1.

Table 1. Photophysical and Stoke's Shift data of the compounds **A1** and **A2** (Aslan et al., 2017).

Comp.	A1	A2
Cons. (mol/L)	2.37 × 10-5	2.37 × 10-5
Absorption, λmax.,nm (logε)	242 (4.9), 269 (4.7), 285 (4.7), 329 (4.7)	241 (4.8), 265 (5.0), 288 (5.0), 352 (5.0)
Excitation, λEx., nm (logε)	309(7.3)	308(7.5)
Emission, λEm., nm (logε)	745(7.4)	407(7.6)
Stoke's shift ΔλST (nm)	436	99

The FT-IR spectra of the **A1** and **A2** exhibit characteristic strong bands in the range of 1220-1150 cm^{-1} and 980-940 cm^{-1}. As shown in figure 7, strong peak in IR spectra of **A1** and **A2** compounds observed in 1703 and 1695 cm^{-1}.

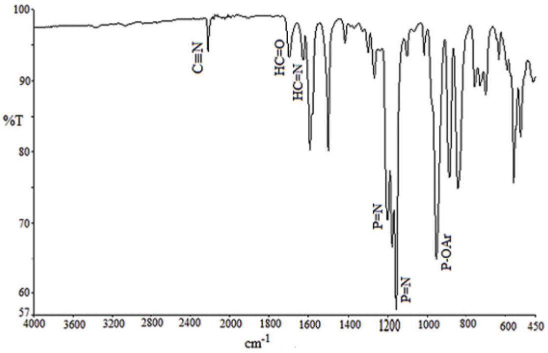

Figure. 7. FTIR spectra of the compounds **A1** and **A2** (Aslan et al., 2017).

The ^{1}H and 31P NMR data of the **A1** and **A2** compounds were given in figure 8, 9, respectively.

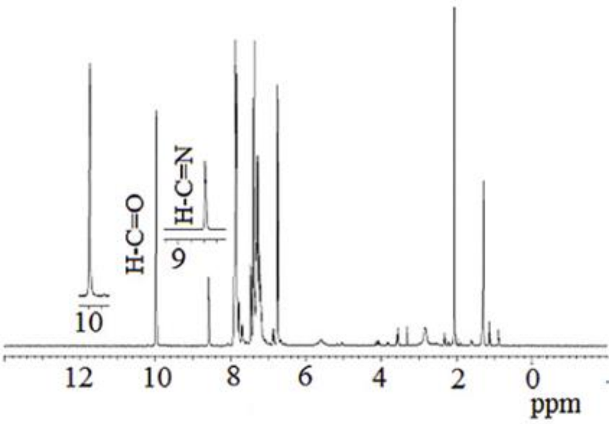

Figure. 8. ^{1}H NMR spectra of the compounds **A1** and **A2** (Aslan et al., 2017).

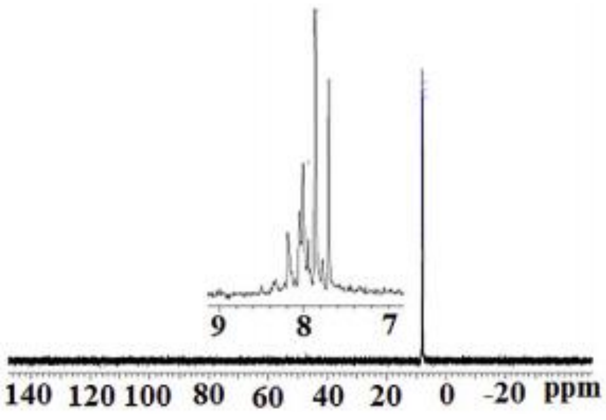

Figure. 9. ^{31}P NMR spectra of the compounds **A1** and **A2** (Aslan et al., 2017).

Mn, Fe, Cu and Zn ions were obtained from the solutions of the salts in water. Compound **A1** was prepared according to the general procedure (0.760 g, 6.960 mmol) as indicated by Aslan et al. (2017). Yield: 0.80 g (97%): mp:185 0C. FTIR (cm^{-1}): 3414 (O-H), 1623 (HC=N), 1205, 1178, 1159 (P=N), 959 (P-O-Aryl). ^{1}H NMR δ (ppm, CDCl3): 8.55 (H-C=N), 7.80-6.50 (Aryl H). ^{31}P NMR δ (ppm): 9.14. Compound **A2** was prepared according to the general procedure (0.760 g, 6.960 mmol) as indicated by Aslan et al. (2017). Yield: 0.64 g (78%):mp:154 0C. FTIR (cm^{-1}): 3414 (O-H), 1625 (HC=N), 1202, 1177 and 1158 (P=N), 955 (P-O-Aryl). ^{1}H NMR δ (ppm, CDCl3): 8.77 (H-C=N), 8.00-6.80(Aryl H). ^{31}P NMR δ (ppm): 8.66 (Aslan et al., 2017).

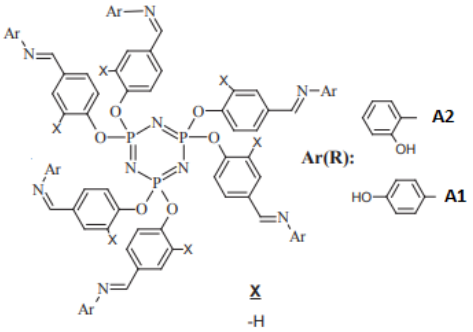

Figure 10. Structure and synthetic route (Aslan et al., 2017).

2.2 Method

2.2.1 Time-Dependent Adsorption Procedures

In 25 mg Adsorbant 1,2,3 and 4 batch reactors, solutions containing 100 mg / L concentration and 50 mL volume of Zn, Fe, Mn and Cu were added and subjected to adsorption test. Adsorption processes were carried out on the 5th, 10th, 15th, 30th, 60th, 90th, 120th, 180th and 240th minutes to observe the time-dependent adsorption efficiency and evaluate the results on various kinetic models. Filtration was then performed. The concentration of ions in the filtrate was determined by AAS. The values obtained were given in the following tables.

Table 2. Adsorption results of metal ions by time of compound **A1**

time, minute	Cu ppm	Fe ppm	Mn ppm	Zn ppm
5	24.720	22.685	25.805	38.700
10	10.034	9.278	10.350	18.268
15	5.057	4.782	5.149	5.964
30	5.148	4.843	5.190	5.890
60	5.139	4.967	5.208	5.851
90	5.188	4.641	5.245	6.302
120	5.175	4.800	5.250	6.007
180	5.101	4.721	5.259	8.775
240	5.027	4.695	5.299	5.940

Table 3. Adsorption results of metal ions by time of compound **A2**

time, minute	Cu ppm	Fe ppm	Mn ppm	Zn ppm
5	23.960	25.150	26.845	32.210
10	10.374	9.842	10.776	11.742
15	5.113	4.832	5.180	5.580
30	5.214	4.956	5.355	5.809
60	5.218	4.979	5.407	5.824
90	5.066	4.717	5.236	5.604
120	5.215	4.831	5.321	5.735
180	5.134	4.894	5.371	5.981
240	5.099	4.764	5.334	5.690

2.2.2 Adsorption Procedures at Different Concentrations of Ions

25 mg Adsorbent was mixed with heavy metal solvents at concentrations of 50, 100, 200, 300, 400 and 500 mg / L. The results are given in the second table. Filtration was carried out at the end of the adsorption time. The concentration of ions in the filtrate was determined by AAS. The results are given in the tables below.

Table 4. Adsorption results of the compound **A1** with respect to the concentration of metal ions

ppm	Cu	Fe	Mn	Zn
50	33.273	35.267	34.867	36.133
100	64.400	65.867	63.533	68.500
200	94.900	131.100	123.500	134.733
300	124.467	164.733	161.100	177.700
400	187.967	248.500	238.800	263.767
500	226.100	307.700	292.700	334.333

Table 5. Adsorption results of the compound **A2** with respect to the concentration of metal ions

ppm	Cu	Fe	Mn	Zn
50	39.033	43.967	41.967	45.133
100	58.700	64.467	62.567	66.267
200	88.667	117.700	115.567	128.500
300	129.167	174.967	169.500	196.000
400	182.067	251.700	239.933	281.000
500	212.467	290.833	276.600	318.067

3. Results and Discussion

3.1 Evaluation of adsorption results of the compound A1

In the 50 mL aqueous solution of 100 mg / L containing 25 mg Cu. Fe. Mn and Zn ions of the compound **A1**. were activated in the 5th. 10th. 15th. 30th. 60th. 90th. 120th. 180th. and 240-minute periods. At the end of these periods. the concentration of ions in the solution was determined. **A1** adsorbed all selected ions and adsorption was completed in 10 minutes. After a period of 10 minutes. the concentration of ions remained constant. The graphs of the obtained values of the tests were given in the following figures.

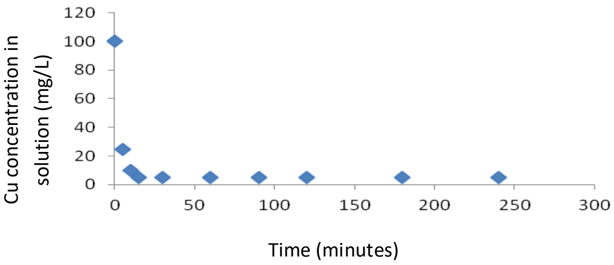

Figure 11. Variation of the concentration of Cu ions in which the compound of A1 is not adsorbed over time.

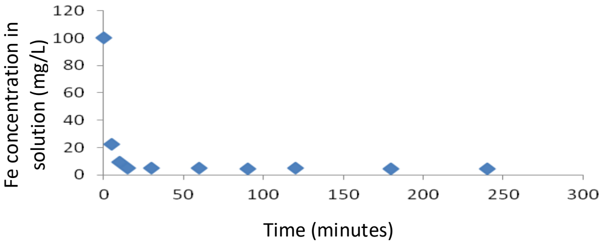

Figure 12. Variation of the concentration of Fe ions in which the compound of A1 is not adsorbed over time.

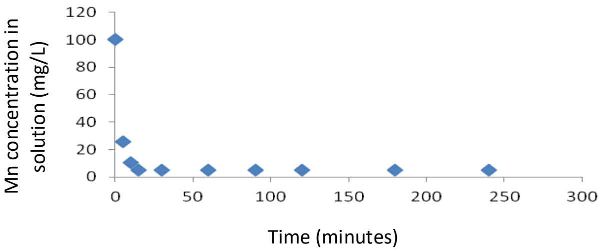

Figure 13. Variation of the concentration of Mn ions in which the compound of A1 is not adsorbed over time.

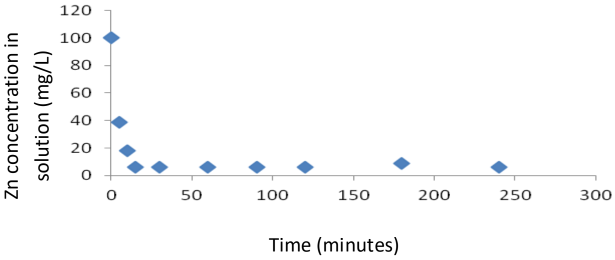

Figure 14. Variation of the concentration of Zn ions in which the compound of A1 is not adsorbed over time.

3.2 Evaluation of adsorption results of the compound A2

In a 50 mL aqueous solution of 100 mg / L containing 25 mg of Cu. Fe. Mn and Zn ions of the compound **A2** was activated at 5. 10. 15. 30. 60. 90. 120. 180. and 240 minutes. At the end of these periods. the concentration of ions in the solution was determined. **A2** adsorbed all selected ions and adsorption was completed in 10 minutes. After a period of 10 minutes. the concentration of ions remained constant. The graphs of the obtained values of the tests were given in the following figures.

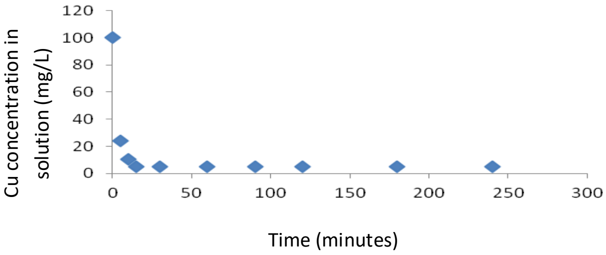

Figure 15. Variation of the concentration of Cu ions in which the A2 compound is not adsorbed over time.

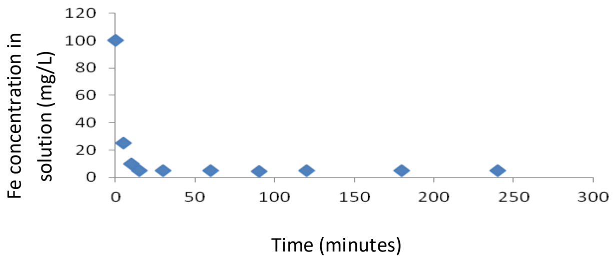

Figure 16. Variation of the concentration of Fe ions in which the A2 compound is not adsorbed over time.

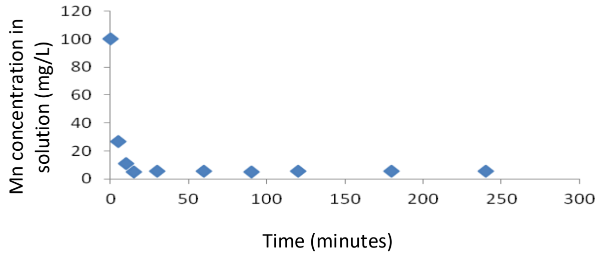

Figure 17. Variation of the concentration of Mn ions in which the A2 compound is not adsorbed over time.

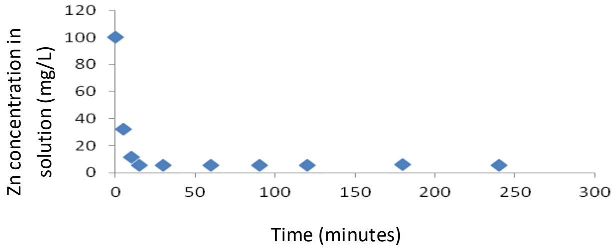

Figure 18. Variation of the concentration of Zn ions in which the A2 compound is not adsorbed over time.

4. Conclusions

Compounds Hexa [4-(4-hydroxy-phenyliminomethyl) phenoxy] cyclotriphosphazene (**A1**) and Hexa [4-(2- hydroxy- phenyliminomethyl) phenoxy] cyclotriphosphazene (A2) which are the imine-bearing organocyclotrifosphazen which we use as adsorbents, were derived from hexa (4-formylphenoxy) cyclotrifosphazen and hexa (2-formyl-phenoxy) cyclotrifosphazen 4-aminophenol and 2-aminophenol. The chemical structure of these compounds is different from each other. Adsorption is available for all metal ions.

Adsorption of metal ions of the compounds was examined according to the time and beginning concentration of metal ions. The selected times are 5, 10, 15,30, 50, 90, 120, 180 and 240 minutes. The initial concentrations of metal ions are 50, 100, 200, 300, 400 and 500 ppm. Adsorbents 25 mg were used in both studies. The analyzes belong to the metal ions remaining in the solution after adsorption.

All compounds adsorbed metal ions which they could adsorb in the first 10 minutes. After this time it was understood that the adsorption did not take place because the concentration of the metal ions was constant. The least metal ion absorbed by all compounds is Zn.

When the initial concentration of metal ions is different the amount of metal adsorbed by the compounds was also different. As the initial concentration of the metal ion increases, the proportion of the amount of metal adsorbed by the compounds increased. Although the amount of compounds is the same in all, the amount of adsorption increases. The amount of metal adsorbed then depends on the initial concentration of the metal.

It was understood that these compounds could be used to remove metal ions.

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