ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

PREPARATION OF POLYACRYLONITRILE GRAFTED ONTO NANO-CLAY FOR REMOVAL OF ALUMINUM FROM AQUEOUS SOLUTIONS

M.Sc. THESIS

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ISTANBUL TEKNİK ÜNİVERSİTESİ ★ LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ

POLİAKRİLONİTRİL AŞILANMIŞ NANO-KİL SENTEZİ VE ALÜMİNYUMUN SULU ORTAMLARDAN UZAKLAŞTIRILMASINDA KULLANILMASI

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Eda Küçük, a M.Sc. student of ITU Graduate School of Science Engineering and Technology student ID 515181006, successfully defended the thesis/dissertation entitled "PREPARATION OF POLYACRYLONITRILE GRAFTED ONTO NANO-CLAY FOR REMOVAL OF ALUMINUM FROM AQUEOUS SOLUTIONS", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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To my dear family,

FOREWORD

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ABBREVIATIONS

ACN **:** Acrylonitrile
EC **:** Electrocoagulation
ECR **:** Eriochrome Cyanine R
EDX **:** Energy Dispersive X-Ray Spectroscopy
FTIR **:** Fourier-Transform Infrared Spectroscopy
PAN **:** Polyacrylonitrile
SEM **:** Scanning Electron Microscopy
TGA **:** Thermogravimetric Analysis
UV-vis **:** Ultraviolet Visible Spectrophotometer
XRD **:** X-Ray Diffraction Analysis

SYMBOLS

C_e	: Concentration
t	: Time
q_e	: The amount of adsorbed adsorbate at equilibrium
q_t	: The amount of adsorbed adsorbate at any time
k_1 , k_2	: The rate constants
k_i	: The diffusion rate constant
q_{exp}	: The capacity as experimentally
q_{theo}	: The capacity as theoretically
R^2	: Correlation coefficient
Q_m	: The maximum adsorption capacity
K_L	: The Langmuir isotherm constant
K_F	: The Freundlich isotherm constant
n	: The Freundlich adsorption intensity
T	: Temperature

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PREPARATION OF POLYACRYLONITRILE GRAFTED ONTO NANO-CLAY FOR REMOVAL OF ALUMINUM FROM AQUEOUS SOLUTIONS

SUMMARY

Heavy metals are extremely carcinogenic and show mutagenic properties when taken into the body. Aluminum (Al) is a toxic metal that is frequently encountered in daily life and can be taken into the body through drinking water, food, drugs and the air we breathe.

Aluminum-based pollutants are found in the wastewater of many industrial sectors such as textile, plastic and food. Removal of toxic pollutants from wastewater has a significant role in terms of health and environment. As a result of many studies on the removal of heavy metals from wastewater, new treatment methods have been discovered. Adsorption is used as the most reliable method preferred for Aluminum among these methods.

Polymeric clays are preferred more often than natural clays as adsorbent in the removal of heavy metal-derived pollutants such as Al from wastewater by adsorption method. Polymeric adsorbents with high adsorption capacity and large surface area are obtained by polymerizing functional groups in the structure of the clay and polymer types with desired properties. It has been determined by the studies on this subject that the adsorption ability of the clay is increased by forming a new sorbent with a suitable polymer.

In this thesis, a new PAN grafted onto nano-clay was synthesized. 1.095 g (0.006 mole) hydrophilic bentonite nanoclay was wetted with 5 mL of distilled water. In a separate beaker, 0.8 g (0.001 mole) ammonium cerium (IV) nitrate used as initiator in redox polymerization was dissolved with 15 mL of distilled water in the presence of 1 mL (0.024 mole) nitric acid. This mixture was added to the wetted clay and the 10 mL (0.152 mole) of acrylonitrile and 15 mL (0.287 mole) of acetonitrile was put the polymerization medium. The graft polymerization was performed at room temperature for 18 h. Pure nano-clay and polymeric nano-clay were characterized by FTIR analysis. In addition, the Aluminum holding capacity of the polymeric nano-clay was characterized spectrophotometrically by sorption studies.

In this study, Eriochrome Cyanine R (ECR) was used as a reagent in Al sorption experiments and all analytical measurements were carried out at pH 6 and using a UV-vis spectrophotometer at 535 nm. Al removal experiments were carried out depending on pH. Furthermore, Al removal studies from aqueous solutions using PAN grafted onto nano-clay as adsorbent were carried out at four different temperatures between 25 °C and 50 °C. In addition, according to the results obtained after the sorption study, kinetic models were applied and adsorption isotherm models were also investigated. When we look at the results of the kinetic models applied in this study, high correlation coefficient values here revealed that the data obtained as a result of the experiment showed a better fit with the pseudo second-order kinetic model.

POLİAKRİLONİTRİL AŞILANMIŞ NANO-KİL SENTEZİ VE ALÜMİNYUMUN SULU ORTAMLARDAN UZAKLAŞTIRILMASINDA KULLANILMASI

ÖZET

Ağır metaller, periyodik tablodaki 5 g.cm^{-3}' ten büyük özağırlığa sahip metaller veya yarı metallerdir. Canlı vücudunda bu ağır metallerden bazılarının eser miktarda bulunması biyoloji ve metabolizma açısından zararlıdır. Vücuda alınan fazla miktardaki ağır metaller toksik etkisi meydana getirmektedir. Kurşun (Pb) ve kadmiyum (Cd) gibi çok toksik metaller insan vücudunun hiç ihtiyaç duymadığı ve bunun yanı sıra mutajenik ve kanserojenik etkiye sahip olan ağır metallerdir. Toksik metallerin vücuda alınması içme suları, gıdalar ve solunan hava gibi birkaç şekilde gerçekleşebilir. Vücuda giren bu metallerin olumsuz etkisi hızlı veya yavaş bir şekilde açığa çıkmaktadır. Ya direkt etki ederek zehirlenme gibi vakalar meydana gelir ya da vücutta yıllar boyunca birikmesi sonucunda farklı hastalıkların oluşmasına yol açar. Hatta hamile kişilerde de yenidoğan bebekleri bu toksik metallerden etkilenir.

Al metali düşük yoğunluklu, korozyona karşı oldukça dirençli, kolaylıkla işlenebilir ve üstün iletkenliğinin olması gibi birçok avantajlı özelliklere sahiptir. Yeryüzünde bolluk açısından üçüncü metal olan IIIA grubuna ait olan Alüminyum (Al) toksik bir metaldir. Günlük hayatta çok sık karşılaşılan bir metal olan Al, yiyecek ve içeceklerden, kullanılan ilaçlardan, yemek pişirme gereçlerinden ve terleme önleyici kozmetik ürünlerinden vücuda alınmaktadır. Canlı vücudunda bulunan Al önemli bir biyolojik işleve sahip değildir bu nedenle vücutta biriktiğinde olumsuz etkileri beraberinde getirmektedir.

Geçmişte yapılan araştırmalar ve çalışmalar sonucunda Al' un tüm organlara özellikle merkezi sinir ve sindirim sistemlerine etki ederek ciddi sağlık sorunlarına yol açtığı anlaşılmıştır. Bu problemlerden en önemlileri Alzheimer ve Parkinson gibi nörodejeneratif kaynaklı hastalıklardır. Bu hastalıklardan ölen kişilerin ardından yapılan araştırmalar sonucunda beyinlerinde çok fazla miktarda Al bulunduğu saptanmıştır. Günlük hayatta Al' un aşırı kullanımı, bunların dışında beyin kanaması, anemi ve ortopedik rahatsızlıkların ortaya çıkmasına da neden olmaktadır.

Büyük çoğunluğunu ağır metallerin oluşturduğu kirleticiler, doğadaki tüm canlılara ve çevreye vermiş olduğu toksik etkilerden dolayı günümüzde büyük endişe kaynağı haline gelmiştir. Bu kirliliğin oluşmasına sebep olan etmenlerden biri de Al kaynaklı sanayi sektörüdür. Bunun nedeni oldukça toksik olan endüstriyel atık suların kanalizasyona boşaltılmadan önce doğru şekilde işlenmemiş veya arıtılmamış olmasıdır. Bahsedilen tüm sebeplerden dolayı ağır metal içeren kirleticilerin atık sulardan uzaklaştırılması sağlık açısından büyük önem arz etmektedir. Bu durum, atık sulardan zararlı metallerin giderilmesi ile ilgili birçok çalışma yapılmasına ve yeni arıtma teknolojilerinin ortaya çıkmasına katkı sağlamıştır.

Ağır metal sınıfına ait olan Al' un sulu çözeltilerden uzaklaştırılması için çeşitli yöntemler kullanılmaktadır. Bu yöntemlerden en yaygın olanları kimyasal çöktürme, iyon değişimi, elektrokoagülasyon, membran filtrasyon ve adsorpsiyondur. Arıtma yöntemlerinin çoğunun kullanılan ekipmanların yüksek maliyetli olması, işlem sonrası oluşan çamurun giderilme zorluğu ve metalin geri dönüştürülememesi gibi dezavantajları bulunmaktadır. Bu nedenle, atık sulardan ya da sulu çözeltilerden Al uzaklaştırmak için maliyeti düşük olan alternatif yöntemlerin kullanımına ihtiyaç duyulmuştur. Bu alternatif yöntemlerden biri de adsorpsiyondur. Bu yöntem, diğer arıtma teknolojileri ile karşılaştırıldığında düşük maliyet, kolay uygulanabilirlik, metalin geri dönüştürülebilirliği, çevre dostu, yüksek verim ve kullanılan adsorbentin çeşitliliği ve yenilenebilir olması gibi çeşitli avantajlara sahiptir.

Adsorpsiyon, akışkan bir sıvı içinde çözünmüş bir veya daha fazla maddenin atomlarını veya moleküllerini kimyasal veya fiziksel bir kuvvetle katı bir yüzeye bağlayarak yüzey konsantrasyonunu artıran bir yapışma kuvveti türüdür. Adsorpsiyon sürecinin gerçekleştiği katı yüzeye "adsorbent" veya " adsorban", katı yüzeye tutunan ve konsantrasyonu artan maddeye "adsorbat" veya "adsorplanan madde" denir. Adsorpsiyon işleminin tersi olarak tanımlanan desorpsiyon da adsorbente tutunan maddelerin ortama geri verilmesi sonucu yüzey konsantrasyonunun azalmasıdır.

Adsorban ile adsorbat arasındaki çekim kuvvetlerine göre fiziksel ve kimyasal olmak üzere iki tür adsorpsiyon vardır. Fizisorpsiyon olarak da bilinen fiziksel adsorpsiyonda, adsorbat ile adsorban arasındaki etkileşimler zayıf Van der Waals kuvvetleridir. Burada adsorbat katı yüzey üzerinde hareket halindedir ve bu tür adsorpsiyon tersinirdir. Fiziksel adsorpsiyon düşük sıcaklıkta gerçekleşir ve aktivasyon enerjisine ihtiyaç duymaz. Çok katmanlı bir adsorpsiyondur. Kimyasal adsorpsiyon aynı zamanda kemisorpsiyon olarak da bilinir ve katı yüzey ile adsorbat arasında yavaş bir şekilde meydana gelen güçlü kimyasal bağ oluşumu ile gerçekleşir. Bu tür adsorpsiyonun geri diönüşümü mümkün değildir. Burada adsorplanan madde adsorban üzerinde hareketsizdir. Kimyasal adsorpsiyonun gerçekleşmesi için aktivasyon enerjisi ve yüksek sıcaklık gereklidir. Bir tür tek tabakalı adsorpsiyondur.

Adsorpsiyon kinetiğine pH, sıcaklık, karıştırma hızı, adsorbanın yüzey alanı ve adsorplanan maddenin çözünürlüğü gibi birçok faktör etki eder. Adsorpsiyonda ortamın pH' ı süreci etkileyen en önemli faktörlerden biridir. Ortamda bulunan H_3O^+ ve OH^- iyonları güçlü bir şekilde adsorbe edilir, bu nedenle ortamdaki diğer iyonların adsorpsiyonu çözeltinin pH' ından etkilenir. Daha güvenilir sorpsiyon sonuçları elde etmek için ortamın pH' ını kontrollü bir şekilde arttırmak gerekmektedir. Genel olarak bakıldığında, sıcaklığın artması ile adsorpsiyon boyutu da artmaktadır. Ekzotermik bir sürece sahip adsorpsiyonda ise, azalan sıcaklık ile adsorpsiyonda artış meydana gelmektedir. Karıştırma hızı da adsorpsiyonu etkileyen bir diğer faktördür. Karıştırma hızının artması ile adsorplanan madde ile adsorban arasındaki etkileşim artar ve bunun sonucunda da adsorpsiyonda artış meydana gelir. Adsorpsiyon işlemi yüzeyde gerçekleşir ve dolayısıyla adsorpsiyon boyutu ile yüzey alanı arasında bir ilişki bulunmaktadır. Adsorbanın geniş yüzey alanına ve büyük gözenek hacmine sahip olması iyi bir adsorpsiyon için olması gereken koşullardır. Adsorpsiyon sürecinde en yaygın kullanılan adsorbentlere doğal killer, aktif karbon, silika (SiO_2), alümina (Al_2O_3) ve zeolitler örnek olarak verilebilir. Adsorpsiyon için doğal killer harika adsorbanlardır. Killerin en önemli özelliklerinden biri geniş yüzey alanına sahip olmasıdır. Ayrıca killer ucuzdur ve üstün iyon değiştirme kapasitesine sahiptir. Kil minerallerinin suyu absorplama özelliğinden dolayı nemli bir yapısı bulunmaktadır. Çeşitli polimerler ile yapılan polimerik killer birçok sentez ve adsorpsiyon sürecinde

avantaj sağlamaktadır. Bir diğer faktör de adsorbatın çözünürlüğüdür. Adsorpsiyonda molekül, çözücüsünden ayrılarak adsorbana tutunur. Adsorbatın çözünürlüğünün yüksek olması katı yüzey ile çözelti arasındaki bağın kuvvetini arttırır. Bu durum da adsorpsiyonun boyutunun artmasını sağlar.

Bu çalışmada Alüminyumun sulu çözeltiden uzaklaştırılması için adsorpsiyon yönteminin uygulanması uygun görülmüştür. Bu tezde, yeni bir PAN aşılanmış nano-kil sorbenti sentezlenmiştir. 1.095 g (0.006 mol) hidrofilik bentonit nanokil, 5 mL distile su ile ıslatıldı. Ayrı bir beherde, redoks polimerizasyonunda başlatıcı olarak kullanılan 0.8 g (0.001 mol) amonyum seryum (IV) nitrat, 1 mL (0.024 mol) nitrik asit varlığında, 15 mL distile su ile çözülmüştür. Bu karışım ıslatılmış kile ilave edildi ve polimerizasyon ortamına 10 mL (0.152 mol) akrilonitril ve 15 mL (0.287 mol) asetonitril konuldu. Aşı polimerizasyonu, oda sıcaklığında 18 saat boyunca gerçekleştirildi. Saf nanokil ve polimerik kil, Fourier Dönüşümlü Kızılötesi Spektroskopisi (FTIR) ile karakterize edilmiştir. Ayrıca, polimerik sorbentin Alüminyum tutma kapasitesi, sorpsiyon çalışmaları ile spektrofotometrik olarak karakterize edilmiştir.

Çalışmanın ilk kısmında, 0.025 g ile 0.15 g arasındaki farklı sorbent miktarları, Al^{3+} çözeltisi ile oda sıcaklığında 24 saat boyunca etkileştirilmiş ve deneysel veriler sonucunda optimum sorbent miktarı 0.050 g olarak bulunmuştur. Tüm sorpsiyon çalışmalarında bu reçine miktarı kullanılmıştır. Sonrasında, 0.050 g sorbent, 2–50 ppm arasındaki farklı Al^{3+} başlangıç konsantrasyonlarındaki çözeltilerle oda sıcaklığında 24 saat boyunca etkileştirilmiştir. Sorbentin maksimum Al tutma kapasitesi 1.43 mg/g olarak bulunmuştur. Tüm adsorpsiyon işlemlerinden sonra süzülen çözeltideki Al konsantrasyonu reaktif olarak eriochrome cyanine R (ECR) kullanılarak pH 6' da, 535 nm dalga boyunda UV-vis spektrofotometre kullanılarak spektrofotometrik yöntemle tayin edilmiştir. Ayrıca Al giderme çalışmaları pH' a bağlı olarak da gerçekleştirilmiştir.

Çalışmanın son kısmında, sentezlenen polimerik kilin sulu çözeltilerdeki Alüminyum adsorpsiyon hızı araştırılmıştır. Kinetik çalışma 25 °C ile 50 °C arasında dört farklı sıcaklıkta gerçekleştirilmiştir. 0.050 g sorbent, Al^{+3} çözeltisi ile etkileştirilmiştir. 2-60 dk. arasında belirlenen farklı aralıklarda alınan numuneler ile zamana karşı kapasite değişimi incelenmiştir. Ayrıca kinetik çalışma sonrasında elde edilen deneysel sonuçlara göre kinetik modeller uygulanmış ve adsorpsiyon izoterm modelleri de araştırılmıştır. Bu çalışmaya uygulanan kinetik modellerin sonuçları karşılaştırıldığında, yalancı birinci mertebe kinetik modelin korelasyon katsayı değerleri (R^2), yalancı ikinci mertebeden kinetik modelin R^2 değerlerinden daha düşüktür. Buradaki yüksek korelasyon katsayı değerleri, deney sonucunda elde edilen verilerin yalancı ikinci dereceden kinetik modele daha iyi uyum gösterdiğini ortaya koymuştur. Bu çalışmada Langmuir ve Freundlich izoterm modelleri incelenmiş olup, deneysel sonuçların Langmuir izoterm modeline uyduğu belirlenmiştir.

Adsorpsiyon işleminden sonra polimerik sorbentin yeniden kullanılabilirliğini araştırmak için desorpsiyon yapılmıştır. Bu çalışma için 0.050 g polimerik kil Al^{3+} çözeltisi ile oda sıcaklığında 2 saat boyunca etkileştirilmiştir. Adsorpsiyon tamamlandıktan sonra, desorpsiyon için Alüminyum yüklü sorbent, 0.1 M NaOH çözeltisi ile oda sıcaklığında 24 saat boyunca etkileştirilmiştir. Desorpsiyon işlemi de tamamlandıktan sonra, bu adsorpsiyon-desorpsiyon süreci toplamda dört kez tekrarlanmıştır. Elde edilen deneysel veriler, adsorpsiyon çalışmalarında PAN aşılı kilin Al uzaklaştırmak için tekrar tekrar kullanılabileceğini göstermiştir.

1. INTRODUCTION

Drinking water and water resources have a vital importance in the life of all living things. Nowadays, with the increasing population, household and industrial wastes, chemical pesticides and fertilizers used in agriculture are the main elements that pollute the water. As a result of the mixing of heavy metal-containing wastes of various industries into the waters, significant health problems and environmental problems have occurred [1]. While toxic heavy metals such as Al, Pb and Hg cause Alzheimer's and Autism diseases, heavy metals such as Mn, Cu and Cd have a major role in the emergence of Parkinson's illness.

About 60 years ago, when it was understood that chemical pollutants have toxic and carcinogenic properties, the removal of heavy metals from water gained great importance [2]. Various methods such as chemical precipitation, adsorption, ion exchange, electrocoagulation and membrane filtration are used to treat wastewater containing heavy metals.

Adsorption is known to be the most effective method for the removal of Aluminum from wastewater. Polymeric adsorbents with higher adsorption capacity and larger surface area are commonly used for Aluminum.

In this study, the adsorption method was utilized to remove Aluminum metal from aqueous solutions. For this aim, polyacrylonitrile grafted onto nano-clay was synthesized as adsorbent and the characterization studies of the prepared samples were carried out by analytical and spectroscopic methods. Furthermore, the capacity of polymeric clay sorbents to remove heavy metals such as Aluminum was researched.

2. THEORY

2.1 Heavy Metals and Their Effects on Human Health and Environment

Metals and metalloids (semimetals) with a specific gravity greater than 5 $g.cm^{-3}$ in the periodic table are generally referred to as ‘’Heavy Metals’’. The presence of small amounts of some heavy metals such as aluminum (Al), zinc (Zn), iron (Fe), copper (Cu) in the human body is necessary for the continuity of biological activities. However, taking these heavy metals into the body more than necessary also causes the metals to have a toxic effect. Some toxic heavy metals such as mercury (Hg), cadmium (Cd), lead (Pb) and arsenic (As), which are much more dangerous than metals in the other group, are not needed by the body at all [3]. Heavy metals in this category have both undeniably carcinogenic effect and mutagenic property. Nevertheless, the mentioned toxic heavy metals can get in the body from outside with the water we drink, the food we eat and the air we take. These metals either act immediately and cause poisoning, or they accumulate in the body and continue their existence for years. In some cases, heavy metals accumulated in the mother's body can be transferred to her child by birth. This can lead to many serious health problems and even death in children [3]. The toxical impact of commonly known heavy metals on health are shown in Table 2.1 [3].

Table 2.1 : The toxic influence of commonly known heavy metals on health.

Toxic Effect on The Health	Heavy Metals
Necessary	Fe, Zn, Cu, Mn, Al and Cr
Unnecessary	Ba, Li and Zr
Less Toxic	Al and Sn
Very Toxic	Pb, Hg, As and Cd

Serious health problems occur in humans when exposed to these heavy metals, which are extremely toxic even in very small quantities. It can be said that determining the extent of health problems caused by heavy metals depends on parameters such as dosage, time, nature and route in terms of exposure [4]. Heavy metals such as Mn, Cu, Fe, Hg, Cd in the structure of the amalgam used in dental treatment are thought to

bring about Parkinson's illness. Alzheimer's and Autism emerge as a result of damaging the brain of heavy metals such as Al, Pb and Hg. In addition to these, Al also causes allergic disorders. Several heavy metals (Pb, Hg, Ta and Cd) also give rise to problems such as excessive mobility, difficulty focusing and hypoglycemia in individuals. Heavy metals such as Pb and As play a role in the occurrence of neuritis disease [5]. Heavy metals can be listed according to their toxicity characteristics in living systems as follows: Hg> Cu> Zn> Ni> Pb> Cd> Cr> Sn> Fe> Mn> Al [6-8].

Heavy metals stand out as a major problem in the pollution of the environment due to their toxicity as they are found in living things (humans, animals and plants) and foods [3]. Environmental pollution is mostly caused by heavy metals emerging as a result of soil-based activities, wastewater, industrial wastes and traffic. Most of the heavy metals that are taken by eating, drinking and breathing into the human body are soil sourced. The reason for this is that heavy metals such as Zn, Cu, Pb and Cd, which pose many dangers to human health, contaminate the soil [9,10]. Plants absorb heavy metals in the soil into their textures in the process of maintaining their biological activities. As people obtain most of their food from the soil, they take these metals into their bodies by way of plants. Moreover, people can be affected by various heavy metals found in water directly with tap water (Cu) and drinking water (Ni), and indirectly with groundwater (sewage), rainwater and car wash water (Zn) [11].

2.2 General Information About Aluminum

Aluminum, whose chemical sign is Al, belongs to the IIIA group in the periodic table. It is also a toxic metal with an atomic mass of 26.98 and atomic number 13 [12]. The pure state of Aluminum can be described as gray, bright and ductile as shown in Figure 2.1 [13]. When looking at the specific gravity of Al element (2.55-2.80), this metal is light, but after oxygen (49.5%) and silicon elements (26%), it expresses almost 8% of the earth's crust [14]. This situation has enabled Al to be the third metal in terms of its abundance in the earth [14].

Aluminum is the metal that is frequently utilized in every moment of quotidian vita and has the highest dispersion feature in the environment. Al is passed into the body through nutrients, drinks, medicines and the environment. When this metal is taken into the body, it may cause harmful influences because Aluminum cannot be said to have an significant physiological function in living organisms [15].

Approximately 300 minerals contain the element Aluminum, and the silicate and oxide compounds consisting of Al has very steadfast in terms of chemically. With the discovery of a technique by the Henri Sainte-Claire Deville (French chemist) in 1854, large-scale Aluminum production was successfully carried out. After developing this process, the French chemist explained the characteristics, the production method and application areas of this element in his premier book that he published [16].

In addition to these, features such as being machinable, not having high density, being undeniably resistant to corrosion and having superior electrical and thermal conductance provide many advantages to Al. In the publication written by Jules Verne in 1865 with the title "From the earth to the moon", Al is described with the prominent properties of other elements in the periodic table: Al element is explained with phrases such as durable like iron, meltable like copper, white color like silver, light like glass and indestructible like gold. He also stated that Al played a major role in the formation of the main structure of rock fragments and iron was three times heavier than Aluminum compared to its weight [17].

Figure 2.1 : The physical appearance of the pure Aluminum element.

In addition to these works for Al production, many different and successful studies have been carried out from past to present. To give a few examples, firstly, Al was obtained by electrolysis method after dissolving alumina in cryolite in 1886. Another study, in 1888, K. J. Bayer purified alumina by extracting it from bauxite. In the 1960s, among the metals in the group called non-ferrous, Al was the most commonly utilized globally. Today, it still has a wide range of applications such as cooking equipments, anti-perspirant cosmetic products, aircraft and spacecraft, and the construction industry [17].

Aluminum, which exists as a cation in nature, has an oxidation number of +3 (Al^{3+}) and the complexes obtained by Aluminum with many silicates are insoluble in water. The fact that the Aluminum element, which is in the group 3A in the periodic table, has a low atomic radius (0.51 A°) and +3 charge, rises the polarization impact that its adjacent atoms are exposed to. Since Aluminum is also an amphoteric metal, it is likely to create OH^- compounds in water when the working pH interval is 3-8 ($Al^{3+} \rightarrow Al(OH)_4$). Apart from silicates, Aluminum tends to form complexes with nitrogen, oxygen and phosphate (especially organic and inorganic) derivative compounds [18].

2.2.1 Toxicological effects of aluminum

As a result of past researches and studies, it has been understood that Al affects all living things negatively. It is possible for Al to enter all organs and tissues in the human body, especially the centric nervous and digestive systems with kidneys, and to pile up there for many years. Since Al is a neurotoxic metal, the most important diseases caused by Al are neurodegenerative illness. Al absorption is higher in people with kidney problems and babies in the 0-2 age group compared to healthy individuals, which indicates that they may be more prone to neural diseases caused by Al. Today, even though a definitive conclusion cannot be reached, it is thought that Al is the underlying of Alzheimer's and Parkinson's ailments, which are instances of the neurodegenerative diseases. The area of the brain, called the nigro-striatal, is poor in dopamine, leading to Parkinson's dementia. As a result of investigations made after humans who died of this disorder, it was seen that their brains contained a lot of Al [19].

Likewise, studies conducted over the past two decades have shown that the relationship between them was investigated when a large measure of Al was observed in the brains of individuals with Alzheimer illness, as in Parkinson's disease. Figure 2.2 shows the comparison of the Magnetic Resonance (MR) results of the brains of healthy humans and people with Alzheimer's illness [20]. In addition, many works have shown that there is some Al in the brains of healthy individuals who have not been diagnosed with this disorder. However, the presence of this metal even in drinking aqua has caused people to worry about their health and avoid using Aluminum-containing products such as cosmetics, canned drinks, aluminum foil, pots

and packaging produces [14]. The excessive use of this element in our daily life leads to the occurrence of cerebral haemorrhage, anemia, and orthopedic disorders in addition to the aforementioned diseases [21-24].

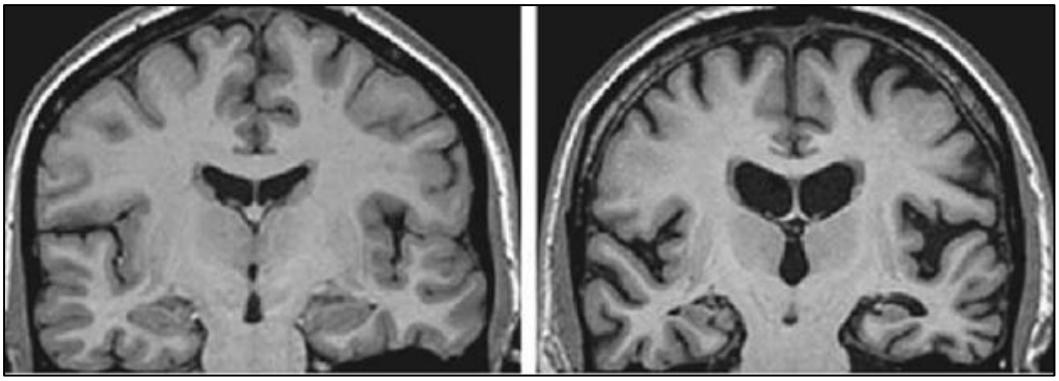

Figure 2.2 : Brain image of a healthy individual on the left and a brain image of an individual with Alzheimer's disease on the right.

Nowadays, Al is found in many foods and beverages. However, the fact that the water we drink contains excessive amounts of this element, which is an inorganic metal, qualifies Al as a toxic heavy metal. Since Al has the property of spontaneous formation even in untreated water, it shows that Al salts used in the treatment process as a coagulant in order to increase the quality of water rise the concentration of Al in the purified water [25]. The limit value for Al has been determined by the World Health Organization (WHO) as 0.2 ppm [26]. Considering the recommended value, removal of Al from water sources by techniques such as electrodialysis, filtration, cation alteration and chemical precipitation is a mandatory process [27]. At the present time, nanotechnology, which has a significant role in purifying water from heavy metals, is a frequently utilized application due to its low cost and high efficiency [28]. Al is known to be present in particulate, hanging and soluble shapes in water. In addition, the situation that causes the color of the water to become cloudy and the cleaning feature is reduced is that the Al concentration in the water is 3.6 - 6 ppm [14,29]. One of the major causes of pollution of water resources such as groundwater, lakes, rivers and seas is the increased amount of Al ion as a result of acid rain [30].

Al is solid in the structure of the soil and the basis of the Al source that people are exposed to is soil pollution [19]. Many vegetables and fruits consumed by humans and animals are obtained from soils containing this metal. Controlling the pH of the soil (4.5-5.0) in food cultivation has a significant impact on human health. If the usage of fertilizers and acid rain causes these soils to acidify, that is, to drop below the given

pH values, the plant enables its roots to absorb the Al dissolved in the water in the soil [31]. As a result of his research, Lione revealed that people take a mean of 3-100 mg of Al with what they eat and drink during the day to their body [32]. Almost one-fifth of Al taken into the body daily is thought to be due to the fact that some cooking pots are made of this metal [33-35]. In addition, it is observed that babies who are breastfed take Al in little quantities from the mother [36]. Some amount of Al taken into the body by inhalation of air or ingestion of eaten food is absorbed in the human body. The remainder can either pile up in the body for many years, or be excreted in urine, which is the most basic way of removing Al from the body [37]. It has been revealed that as a result of aging in humans, the amount of Al rises in direct proportion to age in many organs and tissues such as the brain and lungs [38].

Al taken into the body can sometimes be sourced from cooking utensils or beverage cans [34]. It has been determined that canned cola-like beverages contain 0.1 mg/g, and tea leaves (dry form) 555-1009 µg/g of Al. As a result of the brewing of tea and coffee, the Al concentrations they contain are 4.5-6.0 µg/mL and 0.04-0.30 µg/mL, respectively [39].

2.2.2 Usage areas of aluminum metal

Today, Al is utilized as a significant building material in a wide range of areas from the transportation sector to the construction sector. Al is found in many industrial materials such as home contents, cooking vessels such as stewpots and trays, water heaters, canned drinks and aluminum foil that are frequently used in daily life. In addition, foods with additives such as effervescent powders, frozen foods, ready-made powder mixtures as well as packaging necessaries used in the food industry also contain Al [40]. The presence of Al in sprays used for nasal congestion and in the structure of aspirin and antacid derivative drugs can also be given as example of its usage areas in the pharmacological field. Other application areas are cosmetic products, deodorants and individual care materials utilized as antiperspirants.

Al salts have a great importance in the field of chemistry and their use is possible in many reactions. $AlCl_2$, one of the best known Lewis acids, in Friedel Crafts reactions; methylaluminoxane are widely preferred in polymerization systems of olefins (Zeigler-Natta). $Al_2Cl(OH)_5$ is the active component in care products used to prevent

perspiration [17]. In addition to these, another usage area of these salts is to be used as a coagulant in the process of water purification.

2.3 Methods of Aluminum Removal

Pollutants, the majority of which are composed of heavy metals, cause great fear today due to the inconveniences and dangers they give to all living things and the environment. One of the causes of this pollution is the Al-sourced industrial sector because industrial wastewater is disposed of without being properly processed or treated [23,41,42]. Treatment process is required before discharging the quite toxical wastewater into the sewers [43-45]. For all the aforementioned reasons, separating pollutants such as toxic heavy metals from wastewater requires great importance. This situation has contributed to many studies on the removal of harmful metals from wastewater and also to the emergence of new technologies related to treatment [46]. Various methods are used to remove Al, one of the heavy metals, from aqueous solutions. The most common of these methods are listed as follows [47]:

- Chemical Precipitation
- Ion Exchange
- Electrocoagulation
- Membrane Filtration
- Adsorption

2.3.1 Chemical precipitation

Chemical precipitation, which is one of the treatment techniques, aims to form a precipitate by physically changing the state of suspended or dissolved substances in aqueous solution. In this method, the chemical substance added to the aqueous solution is mixed and the substances desired to precipitate form a precipitate. Thus, heavy metals are separated from the aqueous solution.

Precipitation of metals in aqueous solutions usually occurs in the form of hydroxide. In the equation 2.1, M^{3+} and $(OH)^-$ refer to the dissolved metal ion and precipitation agent, respectively, while $M(OH)_3$ describes to the precipitated metal hydroxide.

$$M^{3+} + 3(OH)^- \leftrightarrow M(OH)_3 \downarrow \quad (2.1)$$

In this method, by adjusting the pH of the aqueous solution to basic conditions, Al^{3+} ion is provided to form precipitate as $Al(OH)_3$. The concentration of Al^{3+} ions in the solution affects the effectiveness of this process. That is, if the Al^{3+} concentration is low (0.001-0.1 g/L), this method is not suitable for treatment, but it causes the method to be much more expensive [48,49].

In addition to the fact that the chemical precipitation method is simple, convenient and reliable as well as the equipment used in this method is inexpensive, making it advantageous to use this method. In addition to these, this technique also has disadvantages. A large amount of sludge is formed as a result of the precipitation process. Increased cost for removing this sludge and damage to the environment are considered as disadvantages of this method.

2.3.2 Ion exchange

Ion exchange is a method based on the displacement between ions bonded to a resin-like solid surface by electrostatic forces and ions with different features that are desired to be removed from the aqueous solution as well as has easy applicability. The exchange here is mostly reversible, and this situation proceeds until the concentrations of the different types of ions in the solution and on the surface reach to equilibrium. Ion exchange is defined as the physicochemical occurrence that happens between an ion exchanger and an aqueous solution [50].

Ion exchangers used to remove unwanted cations and anions in aqueous solution are of two types, cation and anion exchangers. Cation exchangers contain ions with a negative charge to attract cations around them. H^+ and Na^+ ion exchangers are used as cation exchangers. Anion exchangers also contain positively charged ions around them because they want to attract anions. Strong and weak basic anion exchangers can be given as an example to this group. At the present time, resin-derived ion exchangers are widely preferred. The most commonly used natural material of ion exchangers is zeolite, besides, many other materials such as clay, activated carbon coal, cellulose also exhibit ion exchange characteristics.

In the ion exchange process, the treatment capacity and the efficiency of removing unwanted heavy metal are quite high. However, synthetic ion exchange resins used in this technique are not economical and ion exchange capacity decreases after regeneration. This increases the importance of zeolites for this process [51]. Zeolites,

which are natural ion exchangers, are economically viable and there is no change in their capacity even after regenerating a few times.

2.3.3 Electrocoagulation

Electrocoagulation involves the removal of dissolved or suspended contaminants in polluted waters by means of flotation or precipitation methods, in addition to chemical reaction, by using electric current [52]. Coagulation, flotation, adsorption, precipitation and absorption methods constitute the general procedure of EC. The kind of electrode utilized plays a significant role in this treatment technique and Aluminium (Al^{3+}) and Iron (Fe^{3+} or Fe^{2+}) electrodes are commonly preferred. High adsorption capacity, economical and easy accessibility can be listed among the reasons for these two metallic ions to be preferred as electrodes.

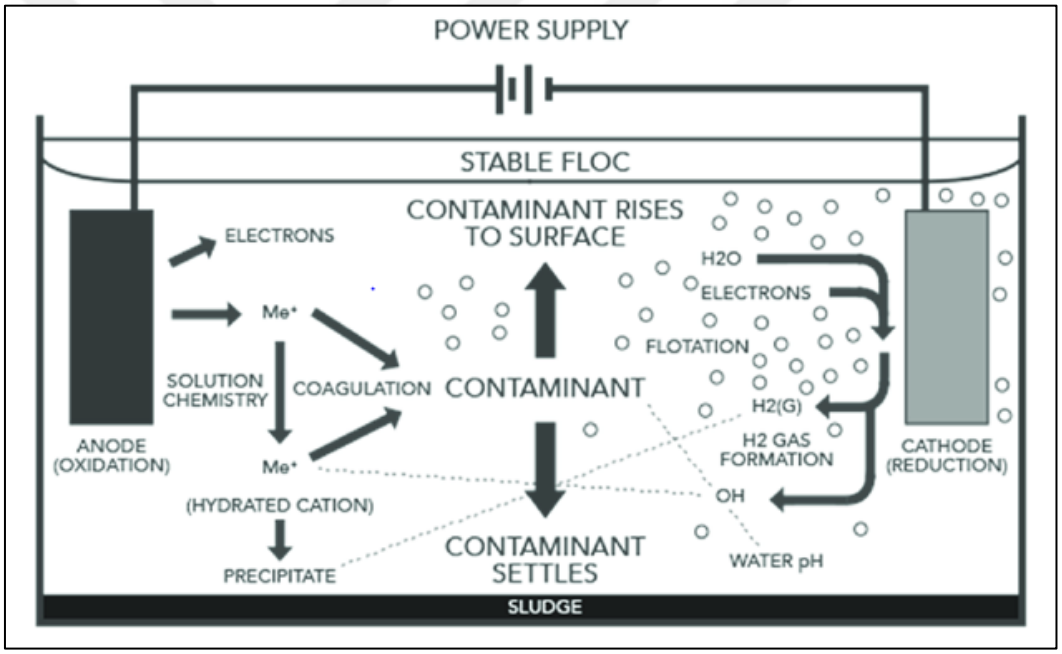

Figure 2.3 : Electrocoagulation process.

During EC process, hydroxyl ions in wastewater interact with Al^{3+}, Fe^{3+} or Fe^{2+} ions dissolved from these electrodes and form important metal hydroxide compounds ($Al(OH)_3$, $Fe(OH)_3$ and $Fe(OH)_2$). It is aimed to remove the impurities in the wastewater to be treated with the metal hydroxides formed by the precipitation method. The coagulation of these ions with contaminants in wastewater provides alumina formation. Thus, wastewater is easily treated from contaminants. The working mechanism of EC used in various industrial areas is given in Figure 2.3 [53].

Electrodes can be oxidized if the soluble substances in the wastewater undergo oxidation. This method is expensive as it requires the use of electricity. When the electrodes are consumed, they should be renewed regularly. Due to these disadvantages, the EC method is not preferred very often for aluminum removal.

2.3.4 Membrane filtration

The purpose of the membrane filtration method, which is a physical separation technique, is to keep the impurities in wastewater with distinct sizes and features with the help of a selective-permeable filter. The pressure difference between the inner and outer sides of the membrane is the repellent force in this method. In order to prevent the particles to be removed from passing through the filter, suitable pore diameter filters in terms of their size are preferred. Correct selection of membrane type is of great importance in order to rise the efficiency and capacity of this filtration process. There are many different processes depending on the pore size of the membrane used in this treatment technology. These are reverse osmosis, ultrafiltration, nanofiltration and microfiltration.

Membrane filtration technology not only reduces production costs, but also allows to increase the quality of the product. On the contrary, the clogging problems experienced during this treatment process and the high cost of the equipment used in this process cause the membrane filtration method not to be preferred very often.

2.3.5 Adsorption

Adsorption is a reliable and widely used heavy metal removal method compared to other methods. The reasons why this method is frequently preferred are its low cost, easy applicability and high efficiency, recyclability of the metal and environmental friendliness as well as the variety and regeneration of the adsorbent used [54].

Adsorption is a type of adhesion force that rises the surface concentration by attaching atoms or molecules of one or more substances dissolved in a fluid liquid to a solid surface by a chemical or physical force. The substance that is attached to the surface and whose concentration increases is called ‘’adsorbate’’ and the solid that adsorption takes place is called ‘’adsorbent’’. The process of decreasing the surface concentration as a result of the separation of the substances attached to the solid surface from the environment is called desorption. In the removal of heavy metals in wastewater

by adsorption, chemical pollutants adhere to a solid surface and are removed from the environment.

Considering the attractive forces between the solid surface and the adsorbed substance, there are two types of adsorption and it is also seen in Figure 2.4 [55].

Physical adsorption, also known as physisorption, is a type of adsorption related only to the surface, in which weak Van der Waals forces are effective between the adsorbate and the adsorbent. The adsorbate is in motion on the solid surface and this adsorption is reversible. The heat of adsorption is quite low (< 10 kcal/mol) and it does not need activation energy. Low temperature is sufficient for physical adsorption to occur. This type of adsorption is multilayered.

Chemical adsorption, also known as chemisorption, occurs by a chemical reaction, usually irreversible, of functional groups between the solid surface and the adsorbate. In chemisorption, stronger chemical bonds are formed and this interaction takes place slowly. The adsorbate is immobile on the solid surface. Heat of adsorption is high (> 40 kcal/mol) compared to physisorption and activation energy is required. High temperature is required for this type of adsorption to occur. It is a type of monolayer adsorption.

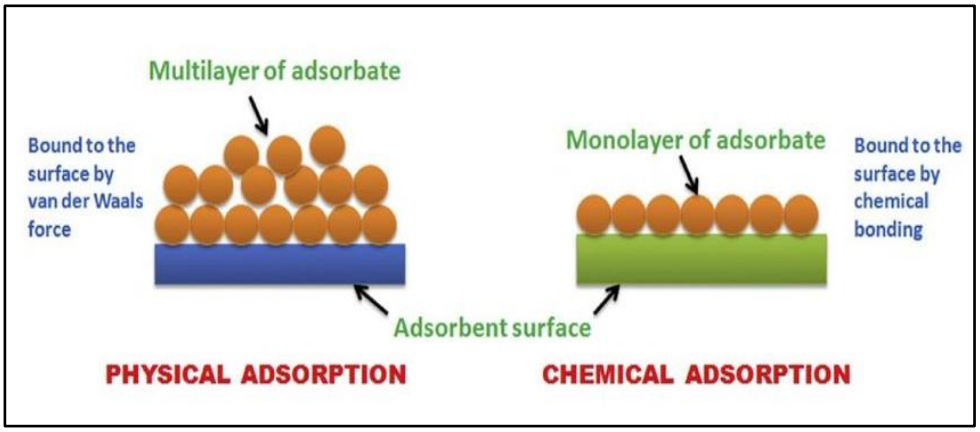

Figure 2.4 : Adsorption types resulting from attractive forces between adsorbent and adsorbate.

There are four main stages in the occurrence of the adsorption process and these steps are representatively explained in Figure 2.5 [56]. In the first step, the substance to be adsorbed (adsorbate) is transported from the bulk fluid to the solid surface (adsorbent). In the second step, the adsorbate diffuses into the pores through the film surrounding the adsorbent. The third step is to adsorb the substance by the

pores and surface of the solid surface. In final step, the adsorbate clings to the solid surface and thus the adsorption process is completed [57].

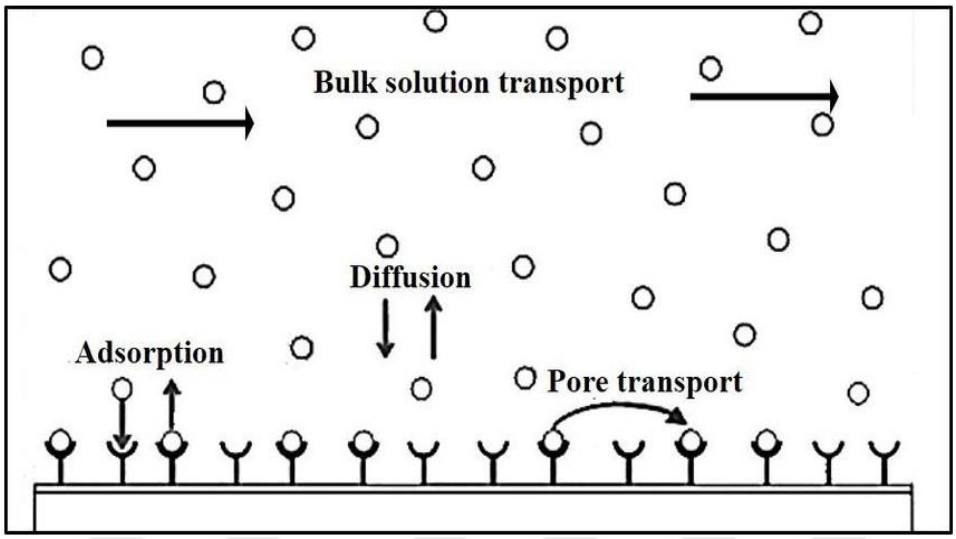

Figure 2.5 : The steps of adsorption process.

Adsorption kinetics is affected by many parameters. These are:

pH: The pH of the environment where the adsorption takes place is one of the most significant factors affecting the process. H_3O^+ and OH^- ions are strongly adsorbed, so the adsorption of other ions in the environment is affected by the pH of the solution. Low pH values are more suitable for the adsorption of organic acids, while high pH values are more efficient for the adsorption of organic bases. Regardless of acid or base, the degree of ionization of the compounds is also a factor affecting the adsorption. In order to obtain more reliable sorption consequences in the adsorption process, it is necessary to increase the pH in a controlled manner.

Temperature: An increase in temperature increases adsorption, while a decline in temperature decreases adsorption. In addition, if adsorption is an exothermic process, the adsorption size rises with decreasing temperature.

Mixing Speed: Another factor affecting the rate of adsorption is the mixing speed. Generally, the increase in adsorption is directly proportional to the increase in mixing speed. Rising mixing speed causes the interaction between adsorbate and solid surface (adsorbent) to rise and thus adsorption increases.

Properties of The Adsorbent: Adsorption is a process that takes place on the surface; hence, there is a proportionality between the size of the adsorption and the surface area. Considering this situation, it is desired that the surface area and pore volume of

the adsorbent should be large and the its structure should be particle-like in order to perform a good adsorption process.

Properties of Adsorbate and Solvent: In the adsorption process, the molecule is separated from its solvent and adheres to the solid surface. In other words, the relationship between the adsorption of a substance and its solubility in the solvent medium is directly proportional. As a result of the high solubility of the adsorbate in the solvent, the bond strength between the solid surface and the solution increases, which allows for greater adsorption. In addition, the solubility of the adsorbed material is a major factor to check the adsorption equilibrium.

2.3.5.1 Adsorption isotherms

The adsorption can also be expressed by analyzing the adsorption isotherms. The adsorption isotherm is the graph that gives the relationship between the amount of adsorbed substance on the solid surface (q_e) and the substance concentration at equilibrium remaining in the solution without being adsorbed (C_e) under constant temperature and pH conditions. Langmuir and Freundlich isotherms are given as examples of the most well-known isotherm models used to determine the adsorption process.

Langmuir Isotherm

Irving Langmuir was the first person to propose the Langmuir isotherm during gas - solid adsorption study on activated carbon selected as adsorbent [58]. There are several assumptions about the Langmuir isotherm: In this model, the surface where the adsorption happens has a homogeneous property. Adsorption occurs as a monolayer in certain parts of the surface, not the entire surface. In addition, in this isotherm, the adsorption energy is the same all over the solid surface, and there is no interaction and steric hindrance between the substances held by the adsorbent. There is no transition between phases [59].

At the beginning of the adsorption, the amount of gas adsorbed by the solid surface starts to rise as the pressure increases and continues in this way until it reaches the maximum point. Even if the pressure increases after this time, the amount of adsorbed gas remains constant. With this process, the point at which the isotherm reaches a plateau can be determined, which indicates that the formation of the monolayer on the

solid surface has been completed. When adsorption, which is also stated as maximum adsorption, reaches the equilibrium saturation point, it is generally better to apply the Langmuir isotherm to chemical adsorption with stronger chemical bonds.

Langmuir isotherm can be expressed in linear (2.3-2.6) and nonlinear (2.2) forms with the equations given below. In the equations, q_e is the amount adsorbed in equilibrium (mg/g), Q_m is the maximum adsorption capacity of the solid surface (mg/g), K_L is the Langmuir constant related to adsorption rate (dm^3/mg) and C_e is the adsorbate equilibrium concentration (mg/L).

When the graph of $\frac{C_e}{q_e}$ $versus$ C_e is drawn, the value of Q_m can be obtained from the slope of the plot and the value of K_L can be calculated from the intercept of the plot.

$$q_e = \frac{Q_m K_L C_e}{1+K_L C_e} \tag{2.2}$$

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m} \tag{2.3}$$

$$\frac{1}{q_e} = \frac{1}{Q_m} + \frac{1}{K_L Q_m C_e} \tag{2.4}$$

$$q_e = Q_m - \frac{q_e}{K_L C_e} \tag{2.5}$$

$$\frac{q_e}{C_e} = K_L Q_m - K_L q_e \tag{2.6}$$

Freundlich Isotherm

This isotherm, revealed by Freundlich (1906), was the first of the models suggested for the explanation of sorption studies [60]. The application of the Freundlich isotherm is possible for both non-ideal and multilayer adsorption occurring on heterogeneous surfaces. This type of isotherm gives the concentration relationship between the amount of adsorbate adsorbed by the solid surface and the substance present in the solution under constant temperature conditions. It is observed that the amount of adsorbed gas rises with increasing pressure. Freundlich isotherm represents physical adsorption involving Van der Waals forces.

$$q_e = K_F C_e^{\frac{1}{n}} \tag{2.7}$$

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \quad (2.8)$$

In the equations given above, both linear (2.8) and non-linear (2.7) forms of Freundlich isotherm are expressed. Here, q_e is the amount of adsorbed substance at equilibrium (mg/g), K_F is the adsorption capacity (mg/g), C_e is the concentration of the substance remaining unadsorbed in the solution at equilibrium (mg/L), n is the adsorption intensity. K_F and n constants depend on parameters such as adsorbate, adsorbent and temperature. When the plot of $\ln q_e$ versus $\ln C_e$ is drawn, the value of n can be calculated from the slope of the graph and the value of K_F can be found from the intercept of the graph.

2.3.5.2 Adsorption kinetic models

Various kinetic models are used to obtain information about the process and mechanism of adsorption. These models help to predict the rate of adsorption, the isotherm model of the process, and the type of interaction that occurs between the adsorbent and the adsorbate [61].

The pseudo first-order model is one of the most preferred kinetic models to find the rate constant of adsorption. This model is expressed by the equation 2.9 given below:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (2.9)$$

q_e and q_t given in the equation are the adsorption capacities (mg/g) at equilibrium and at any time t, respectively, and k_1 is the rate constant of the pseudo first-order equation (min^{-1}). If the equation in 2.9 is integrated under boundary conditions (t=0, q_t=0 and t=t, q_e=q_t), the linear equation is obtained (2.10). When the plot of $\ln(q_e-q_t)$ versus t is drawn, the value of k_1 can be found from the slope of the graph and the value of q_e can be calculated from the intercept of the graph [62].

$$ln(q_e - q_t) = lnq_e - k_1 t \quad (2.10)$$

Equation 2.10 can be rearranged non-linearly (2.11):

$$q_t = q_e(1 - e^{-k_1 t}) \quad (2.11)$$

The pseudo second-order model is another kinetic model frequently used in adsorption studies. This model is expressed by the equation 2.12 given below:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (2.12)$$

In the equation, q_e is the adsorption capacity (mg/g) and q_t is the adsorption capacity (mg/g) at equilibrium and at any time t and k_2 is the rate constant of the pseudo second-order equation (min^{-1}). If the equation in 2.12 is integrated under boundary conditions (t=0, q_t=0 and t=t, q_e=q_t), the linear equation is obtained (2.13).

$$q_t = \frac{q_e{}^2 k_2 t}{q_e k_2 t + 1} \quad (2.13)$$

Equation 2.13 is rearranged to obtain linear form (2.14). When the plot of $\frac{t}{q_t}$ versus t is drawn, the value of q_e can be obtained from the slope of the graph and the value of k_2 can be calculated from the intercept of the graph [62].

$$\frac{t}{q_t} = \frac{1}{k_2 q_e{}^2} + \frac{1}{q_e} t \quad (2.14)$$

Another kinetic model is the intraparticle diffusion model. Weber and Morris suggested this model to explain the diffusion mechanism in the adsorption process [63]. The intraparticle mass transfer diffusion model is expressed by the following equation (2.15):

$$q_t = k_i t^{\frac{1}{2}} + C_i \quad (2.15)$$

Here, k_i is the intraparticle diffusion rate constant (g/(mg.min)) and qt is the amount of substance adsorbed on the adsorbent at any time t (mg/g). When the graph of q_t versus $t^{\frac{1}{2}}$ is drawn, the value of k_i can be found from the slope of the plot.

2.4 Adsorbents

The reason why the adsorption method is widely preferred in removing undesired heavy metals such as Aluminum from aqueous solutions is the properties of the adsorbents used here. Adsorbents should be environmentally friendly, economical, non-toxic, easily obtainable, containing functional groups, insoluble in water and recoverable at the end of the process. Adsorbents are divided into two classes as natural adsorbents and artificial adsorbents.

2.4.1 Natural adsorbents

Natural adsorbents are materials that do not require pre-treatment and are easy to produce. Compared to artificial adsorbents, they are low cost and do not generate large amounts of waste. The only downside is that they are not applicable to all materials.

When their origins are examined, natural adsorbents are divided into two groups: Inorganic adsorbents and organic adsorbents. Zeolite, clay, charcoal and perlite can be given as examples of inorganic adsorbents. Cellulose, resin, chitosan, tea and coffee pulp, various industrial and domestic wastes are also examples of organic adsorbents.

2.4.2 Types of natural adsorbents

2.4.2.1 Zeolites

The meaning of the word zeolite is "Boiling Stone". It is called so because this mineral explodes when heated and breaks into small pieces. Zeolite is one of the most important raw materials used in the chemical industry. Zeolites are aqueous aluminosilicate minerals with a crystalline structure formed by alkali and alkaline earth elements and its structural formula is given in equation 2.16. M in the formula represents alkali and alkaline earth metal and n represents its valence.

$$M_{\frac{x}{n}}\left[(AlO_2)_x(SiO_2)_y\right].zH_2O \qquad (2.16)$$

Zeolites are cheap adsorbents because they have the property of spontaneous formation in nature. They are frequently preferred in the adsorption process because their metal holding capacity is quite high. Zeolites are porous structures consisting of three dimensional networks or lattices containing homogeneous spaces of SiO_4^+ and AlO_4^+ tetrahedra. In Figure 2.6, zeolite is shown in both 3D and basic structure [64]. The high cation exchange capacity of Aluminum and Silicon in the structure of this mineral makes it advantageous.

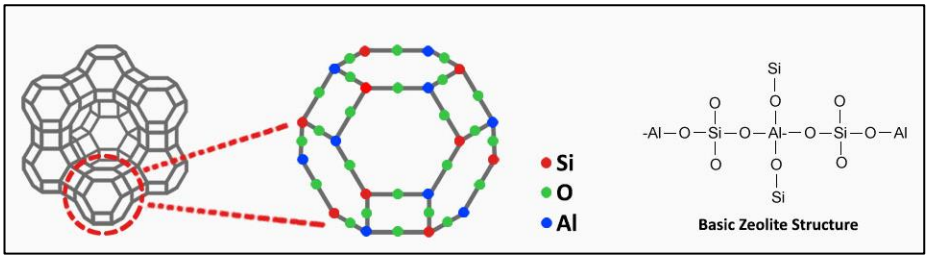

Figure 2.6 : Three-dimensional and simple structure of zeolite.

The disequilibrium created by the minus charges of the four oxygen atoms bonding with Al^{3+} causes excessive negative charge formation in the lattice structure of the zeolite. This leads to a rise in the ion exchange capacity of the zeolites [65].

There are more than 40 natural zeolite species. Analcime, mordenite, erionite, clinoptilolite, ferrierite, phillipsite, and chabazite can be given as examples of the most known zeolite varieties. The most abundant of these in nature is clinoptilolite [66].

Another feature of zeolites is that they have a strong hydrophilic capacity. When the zeolite is interacted with acid, the Si/Al ratio decreases and the hydrophobicity of the material makes better. However, there are also hydrophobic zeolites and their Si/Al ratio is high.

Zeolite minerals have several different characteristics: When heating process is applied, they lose their water molecules in their structure. The reverse is also possible, that is, they must be subject of water vapor in order to recover water molecules. At very high temperatures (> 500 ºC), the hydroxyl groups in the structure of the zeolite are lost. This adsorbent has a low density (1.91-2.30 g/cm^3). Due to the micro-porous structure of zeolite, it has various functions in industry:

- Ion exchanger

- Adsorbent

- Molecular sieve

- Catalyst

Natural zeolites, which have an increasing importance in the industry in the last few years, are used in the removal of pollution in wastewater, purification of oil and natural gas, food additives used in livestock area, prevention of insects and weeds in agriculture, and improving the soil.

2.4.2.2 Clays

Clay is a valuable adsorbent with very small particle sizes (< 2 μm) that occurs spontaneously on earth. Water, silica, alumina and weathering rocks are the main elements that make up the clay structure and also these substances are called hydrated aluminum silicate [67]. The chemical formula of clay is generally expressed by the following equation 2.17.

$$mAl_2O_3.nSiO_2.pH_2O \quad (2.17)$$

Clay minerals are generally a layered structure formed by one or two silica layers with tetrahedral geometry around an aluminium layer with octahedral geometry. The geometrical structure of the two units that make up the basic structure of clay minerals can be seen in Figure 2.7 [68]. Al_2O_3 octehedron and SiO_2 tetrahedron layers combine in various ways to create clay minerals with different properties.

Clay minerals are divided into three groups according to the layer type: kaolinite, micas (exemplarily illite) and smectite (exemplarily montmorillonite). The combination of octahedral and tetrahedral layers forming their structure is given in Figure 2.8 [69]. Kaolinite has a tetrahedral and an octahedral layered structure (or TOT, 1:1) while illite and smectite have two tetrahedral and one octahedral layered structures (or TOT, 2:1). Compared to the other two clay types, it is estimated that the adsorption capacity of montmorillonites is the highest. Because their surface area is larger, their crystal structure is smaller, and their ion exchange ability is higher.

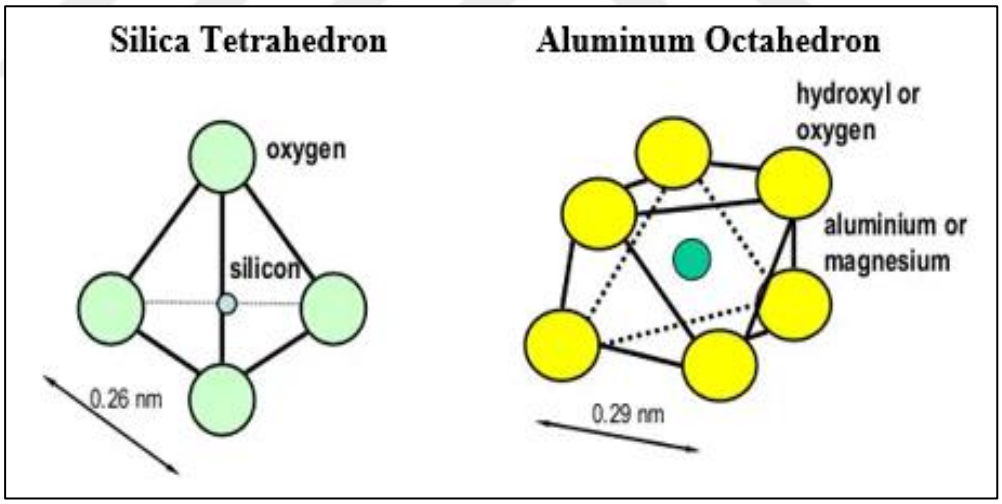

Figure 2.7 : The geometrical structure of Al_2O_3 and SiO_2.

One of the most important features of clay is that it has a large surface area. This feature increases the adsorption capacity of the clay [70]. Another feature of clay is that the net charge of silicate minerals in its structure is negative, which contributes to the adsorption capability of this mineral. The negative charge of the clay is neutralized during the adsorption of compounds with a positive charge, and this situation allows metal ions (such as heavy metals) to be attracted by the clay.

Compared to other natural adsorbents, clays have various application areas due to their many unique properties. Clay raw material has a significant role in dissimilar research fields such as engineering, cosmetics, building necessaries, ceramics, roofing, agriculture, medicine, steel production, oil and paper production.

The use of clays in different areas in industry has made them popular inorganic materials. Clays, which are naturally and abundantly found in nature, are not toxic to humans and the environment. In addition, other important features of this adsorbent type are that it is economical and has a superior ion exchange capacity. Clay minerals draw the attention in many areas because they have different properties in terms of structure and surface, as well as their high adsorption ability. Finally, it has the ability to absorb water due to its clay structure. Due to this feature, clay materials always have a moist structure.

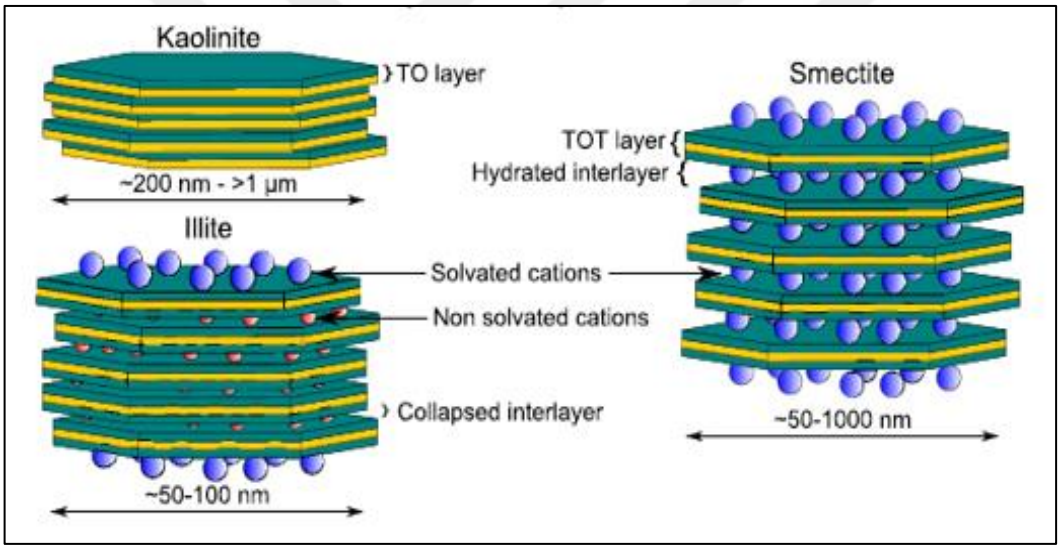

Figure 2.8 : The layers that make up the structure of the clay types.

Clays, principally montmorillonite, are the most common adsorbents used to remove toxic heavy metals such as Zn^{2+}, Al^{3+} and Pb^{2+} from aqueous solutions, and many studies have been carried out in recent years [71-73]. The majority of the studies have shown that the concentration of the metal must be increased in order to increase the adsorbed amount of the metal to be removed. In addition, pH is one of the important factors affecting adsorption. Many studies have demonstrated that the adsorbed amount of metals increases up to pH 6 values, but when the pH value rises above 8, precipitate formation is observed and adsorption decreases. This indicates that the suitable pH value for the adsorption of most metals is 6.

2.4.3 Polymeric clays

Although the use of natural clay is more preferred when compared to other adsorbents in the removal of contaminants such as toxic heavy metals and dyes from aqueous solutions, the modified clays obtained as a result of improving some of their properties, such as adsorption ability and surface area, by several methods, become more efficient for these studies. Many studies have been conducted on the effectiveness of natural clay and modified clay used as adsorbent in adsorption studies.

Polymeric clays are a type of material obtained by combining polymers with desired properties with various clay minerals. The excellent compatibility of the clay raw material with polymers has increased the interest in the use of polymeric clays as adsorbent in the last few years.

Clay raw material has limitations such as low adsorption ability against organic substances and difficult recovery from aqueous solutions. In order to eliminate these limiting situations, polymeric clays with advantageous features have been developed by combining clay minerals with properties such as non-toxic, inexpensive and large surface area with polymer types with especially high adsorption capacity.

Various functional groups in the structure of clay minerals can be attached to the interlayer spaces or on the surface by polymerizing many polymer types [74,75]. Thus, a special interaction occurs between the clay modified with polymer and the contaminants to be removed, and a high-capacity adsorption takes place. It has been determined that the most beneficial method to rise the adsorption capacity of the clay mineral is to modify it with a suitable polymer [76].

2.5 Acrylonitrile

2.5.1 General information about ACN

Acrylonitrile is an organic compound with a chemical formula of C_3H_3N containing a nitrile functional group attached to the vinyl group, and its chemical structure is shown in Figure 2.9. Acrylonitrile can be named in many ways, such as vinyl cyanide, 2-propennitrile, propylene nitrile, and propenoic acid nitrile. The presence of the cyano group in the structure of acrylonitrile provides an opportunity for the preparation of many different chemical substances from this compound.

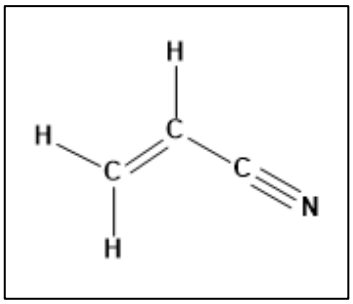

Figure 2.9 : Chemical structure of ACN.

It is a colorless and flammable liquid with a molecular weight of 53.06. Even low amounts of acrylonitrile can be toxic. It is lightly soluble in water but completely soluble in most organic solvents. If the vapor of acrylonitrile interacts with the flame, an explosion will occur. As a result, toxic gases such as carbon monoxide, hydrogen cyanide and nitrogen oxides which are harmful to human health and the environment are released. Acrylonitrile can enter the body mostly by inhalation. In addition, it has been determined that it can be exposed through derm contact and digeston. Other significant physical features to know about acrylonitrile are summarized in Table 2.2 [77].

French Charles Moureu was the first chemist to synthesize acrylonitrile (in 1893) [78]. Acrylonitrile can be used directly in chemical syntheses as well as purified by fractionation method to remove small amounts of water and impurities before use. As acrylonitrile can be easily polymerized, it is frequently used to obtain polyacrylonitrile (PAN) and acrylonitrile butadiene styrene (ABS).

Table 2.2 : Physical properties of ACN.

Physical Characteristics	Values
Molecular Weight	53.06
Density	0.8004 g/cm^3 at 25 °C
Polar Surface Area	27.76 dyn/cm at 15.1 °C
Freezing Point	-83° to -84 °C
Boiling Point	77.3 °C
Melting Point	-83.5 °C
Flash Point	-1 °C
Surface Tension	23.8 Å^2
pH	6.0-7.5

In 1950, DuPont explored acrylic fiber, which can be the raw material of many industrial products, and named it Orlon. The discovery of this new material has increased the utilization of acrylonitrile [79]. Therefore, nowadays, acrylonitrile has become one of the most frequently used petroleum-derived raw materials in the textile and plastic industries and acrylic fiber can be seen in Figure 2.10 [80].

Acrylic fiber production such as carpet, blanket, yarn, electronic products such as telephone, computer and car parts are some of its usage areas. Apart from these, it is also widely utilized in materials used to cover surfaces, in containers where food and beverages are placed, and in adhesive products.

Figure 2.10 : Acrylic fiber obtained from acrylonitrile.

2.5.2 Polymerization of ACN

One of the most fundamental reactions of acrylonitrile is its polymerization. The initiators used for the polymerization of acrylonitrile are light, free radicals and some bases. Especially when light is chosen as the initiator, polymerization occurs exothermically without an inhibitor and free radical polymerization of acrylonitrile is given in Figure 2.11. Also, this polymerization is usually terminated by air.

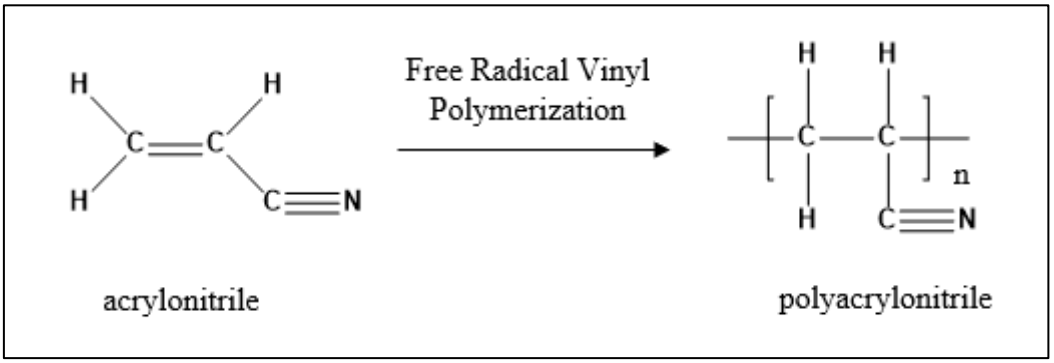

Figure 2.11 : Polymerization of ACN.

PAN, whose chemical structure can be seen in Figure 2.12, is a white colour, water-insoluble, synthetic and semi-crystalline polymer type. Polyacrylonitrile is also called polyvinyl cyanide and Creslan 61. Although PAN has thermoplastic properties, it degrades before melting. The most common use of PAN in fiber making in the textile industry is due to its superior chemical and physical features.

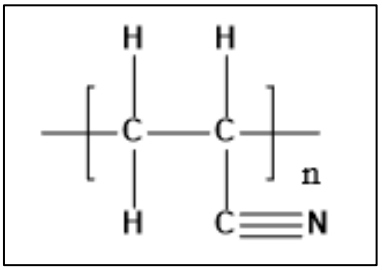

Figure 2.12 : Chemical structure of PAN.

Polyacrylonitriles are the most durable polymers and do not deteriorate with sunlight and UV rays. In addition, PAN, which has an inert structure, is known to resist many organic solvents as well as most acids. Fibers produced from polyacrylonitrile are similar to natural wool due to their soft, not easily broken and warm-keeping characteristics. Fibers are used in various fields such as yacht sails, tennis and badminton rackets, missiles and airplanes, gas filtration systems.

3. EXPERIMENTAL PART

3.1 Materials

Hydrophilic bentonite nanoclay (Aldrich), Aluminum nitrate nanohydrate (Merck), Eriochrome cyanine R (Merck), Ammonium cerrium (IV) nitrate (Fluka), acrylonitrile (Aldrich), asetonitrile (Merck), NaOH (Fluka) and other chemicals were supplied commercially.

3.2 Instruments

FT-IR Spektrophotometer (Nicholet 380), UV-vis Spektrophotometer (Perkin Elmer Lambda 25), TGA (Shimadzu TA-60WS), SEM, XRD (Rigaku D/Max-2200/PC), EDX, shaker (Edmund Bühler KS-15), ultrasonic bath (Bandelin Sonorex) and magnetic stirrer.

3.3 Preparation of the PAN Grafted onto Nano-Clay

1.095 g (0.006 mole) of hydrophilic bentonite nanoclay was wetted with 5 ml of distilled water. In a separate beaker, 0.8 g (0.001 mole) of ammonium cerium (IV) nitrate used as initiator in redox polymerization was dissolved with 15 ml of distilled water in the presence of 1 ml (0.024 mole) of nitric acid. This mixture was added to the wetted clay and stirred with ultrasonic bath about 5 minute. And then 10 mL (0.152 mole) of acrylonitrile and 15 ml (0.287 mole) of acetonitrile was put the polymerization medium and stirred with magnetic stirrer. The redox polymerization was performed at room temperature for 18 hours. Then, 50 mL (0.646 mole) of DMF was added into PAN grafted clay and stirred for 2 hours. After that, polyacrylonitrile grafted onto nano-clay was filtrated and washed with DMF, excess of water and acetone respectively to separete soluble organic and inorganic contaminants. PAN grafted onto nano-clay was dried under vacuum at 40 °C for about 18 h. 4.29 g of the product was obtained.

3.4 Aluminum Sorption Studies of the PAN Grafted onto Nano-Clay

3.4.1 Determination of the optimum amount of the sorbent

Sorption experiments of the Aluminum on the polyacrylonitrile grafted onto nano-clay were investigated in a batch system. In order to find the optimum amount of sorbent, different amounts of sorbent between 0.025 g and 0.15 g were interacted with 10 mL of 20 ppm Al^{3+} solution and stirred at 100 rpm in a shaker at room temperature for 24 hours. After the adsorption process, the filtered solutions were diluted appropratiate amounts for determination of the Al^{3+} ions by colorimetrically at 535 nm using 0.1 M eriochrome cyanine R (ECR) as a reagent at pH 6.

3.4.2 Determination of the Aluminum sorption capacities

After determining the appropriate amount of polymeric nano-clay, 0.05 g of sorbent was reacted with 10 mL of Al^{3+} solution at different concentrations between 2–50 ppm at 100 rpm in a shaker at room temperature for 24 hours. After the adsorption process complete, Aluminum adsorbed sorbents were filtered and sorption capacities of the PAN grafted clay sorbents were examined colorimetrically as described above.

3.4.3 Effect of pH onto Aluminum sorption capacities

For this purpose, 20 ppm Al solutions were prepared by using buffer solutions with pH 3, 6 and 9. 0.10 g of sorbents were interacted with 10 mL of Al solutions for 24 h at room temperature. Aluminum sorption capacities of the sorbents were found spectrophotometrically as described above.

3.4.4 Aluminum sorption kinetics

0.05 g of sorbent was interacted with 10 mL of 2 ppm Al^{3+} solution at 25 °C for different times between 2-60 minutes using magnetic stirrer at 400 rpm. Then each solution was filtered and diluted. Residual Aluminum concentrations of the solutions were determined by UV-vis spectroscopy as described above.

3.4.5 Effect of temperature on the Aluminum sorption

Aluminum sorption capacities of the PAN grafted onto nano-clay were examined at four different temperatures between 25 °C and 50 °C. Also, kinetic studies were investigated depending on temperature.

3.4.6 Regeneration of the Aluminum loaded sorbent

Desorption studies were performed to investigate the reusability of the sorbent after the adsorption process. For this study, 0.05 g of sorbent was interacted with 10 mL of 20 ppm Al^{3+} solution at 100 rpm in a shaker at room temperature for 2 hours. After the adsorption process, this mixture was filtrated and dried under vacuum. Aluminum loaded sorbent was added into 10 mL of 0.1 M NaOH solution and stirred with an orbital shaker at room temperature for 24 hours. And then, this mixture was filtrated and determined Aluminum quantity described before.

Desorbed sorbent was completely dried, this adsorption-desorption process was repeated four times. To determine desorption quantity of the sorbent, 0.01 M of Aluminum solution was prepared in 0.10 M NaOH and was determined absorbance at 535 nm. This value was used to calculate desorption capacity of the sorbent.

3.5 Aluminum Sorption Capacity of the Pure Nano-Clay

To compare sorption capacity of the sorbent against the pure clay, 0.05 g nano-clay was interacted with 10 mL of 20 ppm Al^{3+} solutions at room temperature for 24 hours. After the adsorption process, the solution was filtered and residual Aluminum concentration was determined colorimetrically described above.

4. RESULTS and DISCUSSION

4.1 Preparation of the PAN Grafted onto Nano-Clay

In this study, polyacrylonitrile (PAN) was grafted onto nano-clay using redox polymerization method. For this purpose, wetted nano-clay firstly intereacted with ammonium cerium (IV) nitrate as initiator in the presence of nitric acid and acrylonitrile was added to this mixture under nitrogen medium (Fig. 4.1).

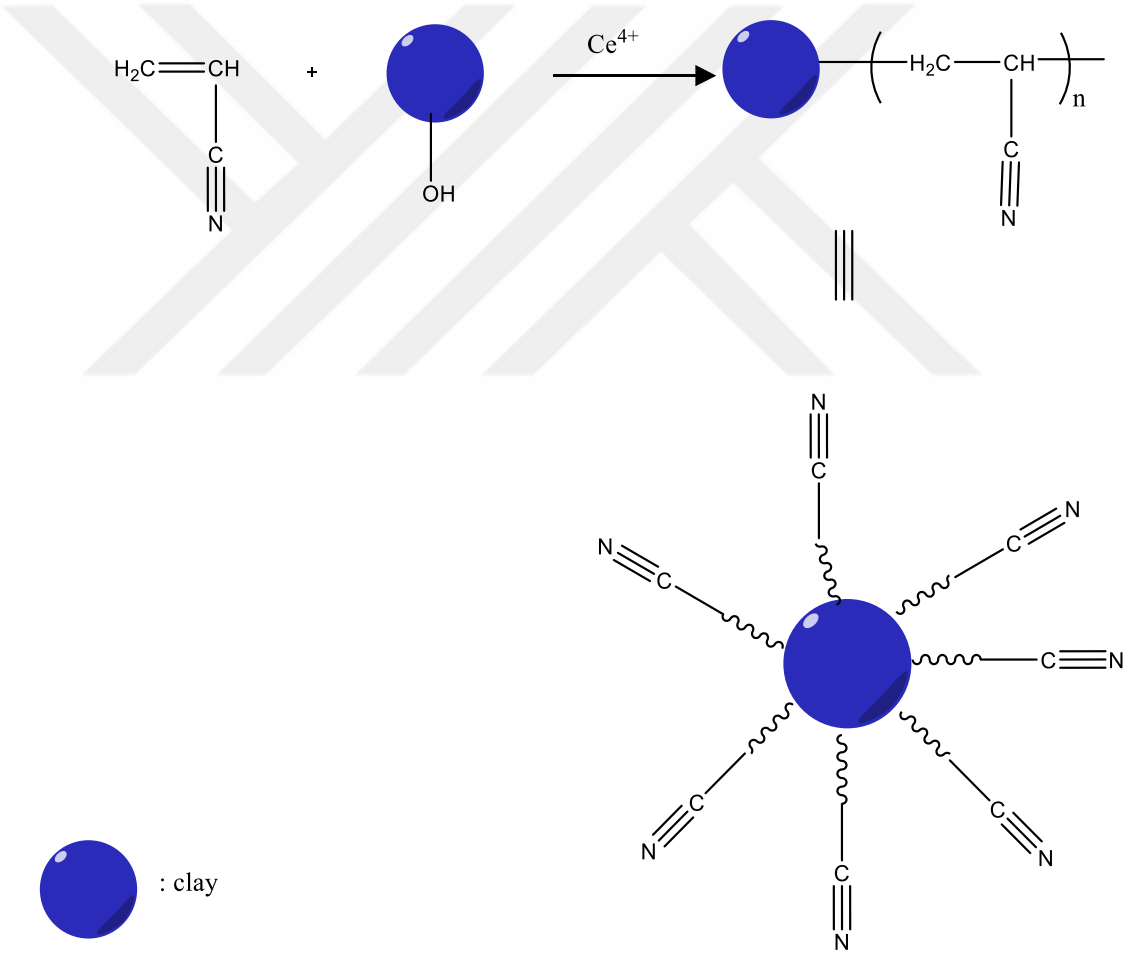

Figure 4.1 : Preparation of the PAN grafted onto nano-clay.

Graft polymerization was preceded for 18 h at room temperature. At the end of polymerization, PAN grafted nano-clay yield was found as 4.29 g and grafting degree was calculated using equation 4.1 below:

$$GP = \left[\frac{(m_{gf} - m_0)}{m_0}\right] x\ 100\% \qquad (4.1)$$

where, GP, m_0 and m_{gf} are grafting degree, initial weight of nano-clay and PAN grafted of nano-clay weight, respectively.

Spectroscopic characterization of the sorbent was investigated with FTIR (Fig. 4.2). The OH peaks between 3300 and 3600 cm^{-1} belongs to the stretching vibration of Si-OH group and also OH bending band is observed at 983 cm^{-1}. Si–O shows bending vibration peak at 510 cm^{-1} and in the FTIR spectra of the nano-clay (Fig. 4.2), the peak was observed at 1632 cm^{-1} belong bending vibration of water molecules in clay structure. At 1423 cm^{-1}, it shows the vibration frequency of the CO_3 group. After grafting PAN onto nano-clay, characteristic C≡N stretching vibration was observed at 2242 cm^{-1}. Also, described peaks in clay shift after grafting polymerization.

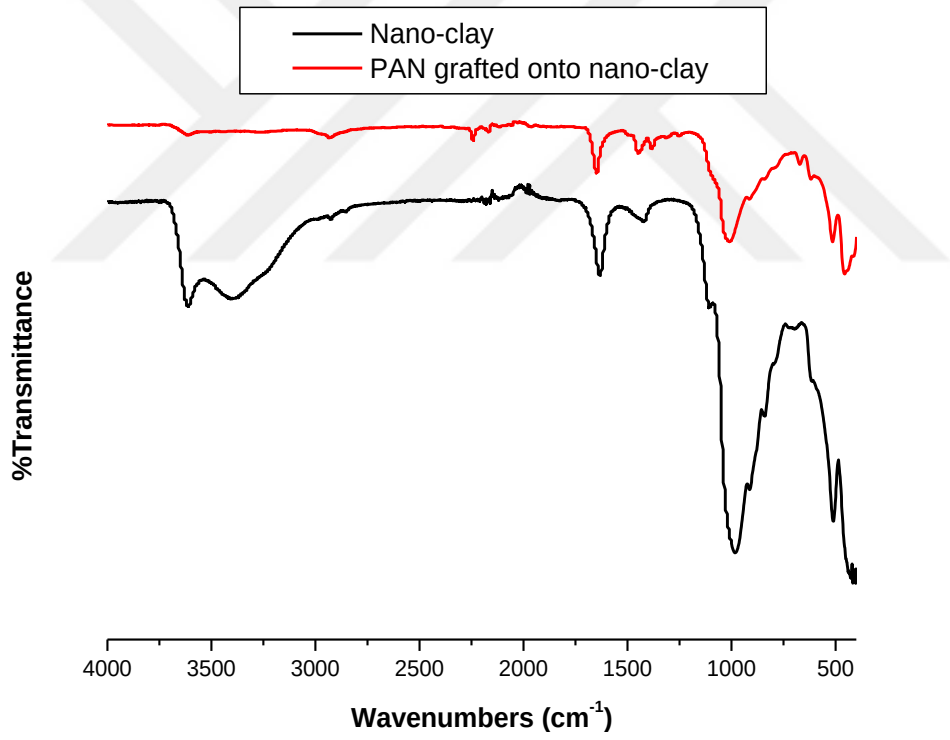

Figure 4.2 : The FTIR spectra of nano-clay and PAN grafted onto nano-clay.

4.2 Aluminum Adsorption Experiments of the Sorbent

Aluminum nitrate nonahydrate salt was used in the sorption experiments. Aluminum sorption experiments of the sorbent were investigated depending on different initial concentrations of Aluminum pH and temperature. Also, some toxic cations sorption properties of the sorbent were studied. Aluminum sorption capacities of the sorbent

was found calculated using equation 4.2 given below colorimetrically at 535 nm using eriochrome cyanine R (ECR) method [81].

$$q_e = V(C_0 - C_t)/m \quad (4.2)$$

where, q_e, C and C_t are amount of adsorbed Aluminum ion per gram of the sorbent (mg/g), initial concentration of metal ion solution (ppm) and concentration of metal ion solution (ppm) at time t, respectively. V is volume of metal ion solution (mL) and m is mass of the sorbent (g) [82].

4.3 Determination of the Optimum Amount of the Sorbent

In this study, to determine sorbent dosage on Aluminum sorption was studied different amounts of the sorbent (25-150 mg) and 10 mL Al^{3+} solutions (20 ppm) in non-buffered conditions were interacted with the different weight of sorbents.

The Aluminum sorption capacities were studied as a function of the sorbent amount. And capacities against to sorbent amounts were given in Figure 4.3. The highest sorption values were found as 50 mg sorbent. Therefore, this amount of the sorbent was used in the sorption experiments.

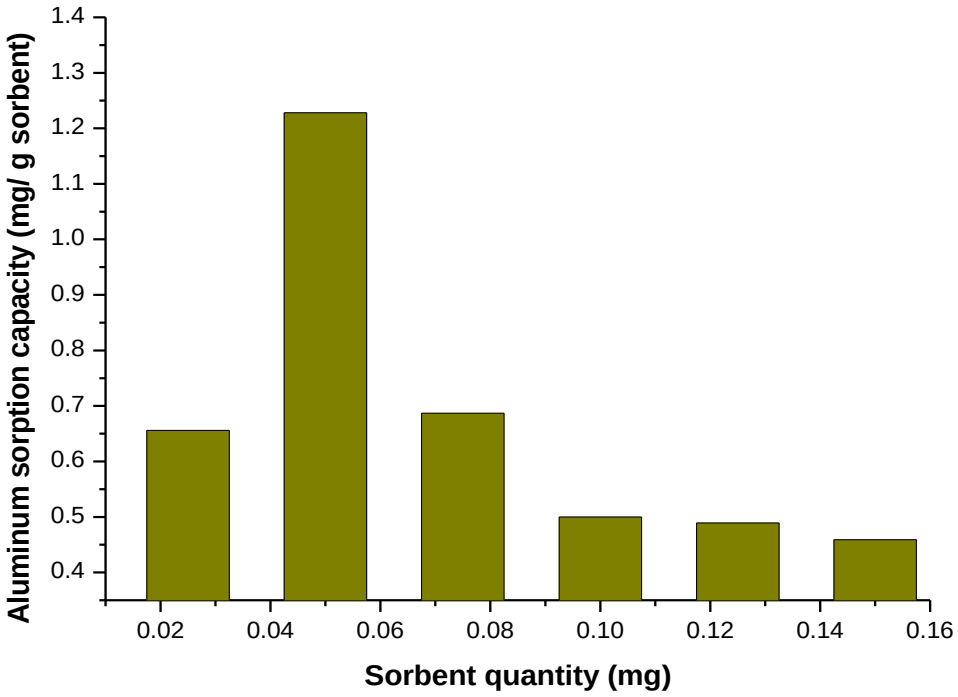

Figure 4.3 : Aluminum sorption capacities of the sorbent according to the sorbent dosage.

4.4 Aluminum Sorption Capacity of the Sorbent

To determine effect of initial Aluminum concentration, this sorbent was interacted with depending on different initial Al^{3+} solutions (2-50 ppm) in non-buffered conditions at room temperature for 24 h.

According to the Figure 4.4 and Table 4.1, Al^{3+} sorption capacity of the sorbent increases increasing Aluminum concentration and maximum loading capacity of the sorbent was found 1.43 mg Aluminum per gram sorbent.

Table 4.1 : Aluminum sorption capacity of the sorbent.

Concentration (ppm)	Capacity (mg Al/g sorbent)
2	0.330
5	0.463
10	0.583
20	1.430
50	1.426

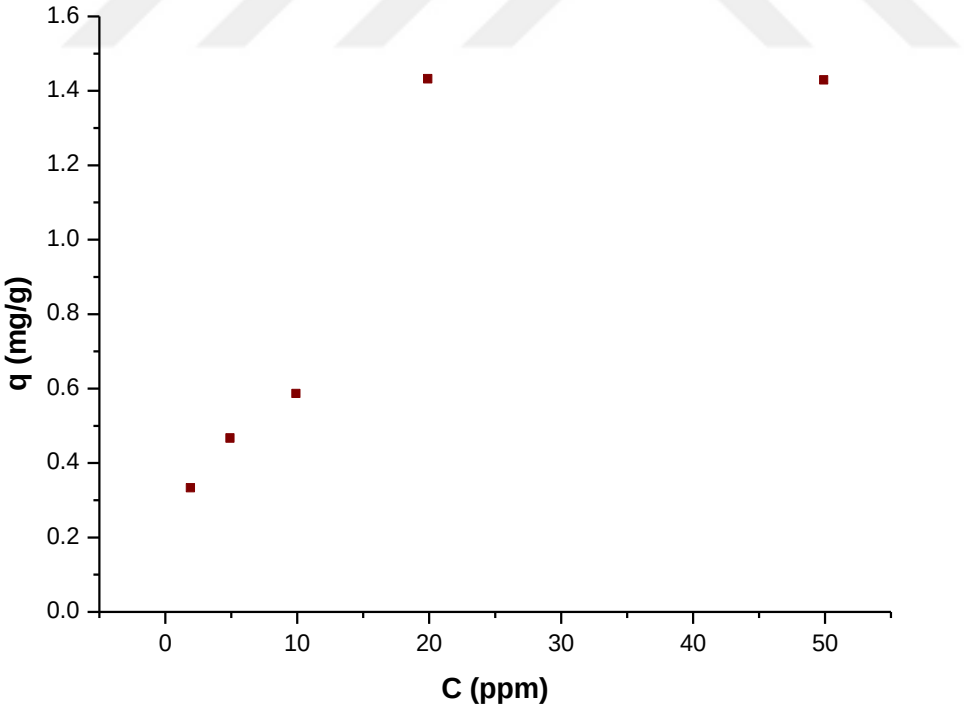

Figure 4.4 : The plot versus initial Al^{3+} concentration to capacity.

pH depending sorption measurements were carried out at the pH range of 3.0-9.0. According to literature, increasing pH value Al precipitation occurs [83].

Considering the information obtained as a result of the pH experiments in Table 4.2, Aluminum sorption capacities do not change between pH 3 and 6. Also, these values are near in neutral condition. But, sorption capacity value was found 2.7421 mg Al/g sorbent at pH 9. At higher pH value Aluminum precipitation occurs, therefore Al^{3+} sorption capacity is higher than low pH values.

Table 4.2 : Aluminum sorption capacities of sorbent depending on pH.

pH	Capacity (mg Al/g sorbent)
3	1.5485
6	1.410
9	2.7421

4.5 Morphological Characterization of the Sorbent

Morphological characterization of the materials was carried out SEM and EDX analysis. The SEM images in Figure 4.5 are of nano-clay, PAN grafted onto nano-clay and Aluminum adsorbed PAN grafted onto nano-clay. When the SEM images were examined, the granular nano-clay samples were inoculated with PAN, and the granular structure disappeared and the polymer layer accumulated on the clay. After the Aluminum was adsorbed, heterogeneous condensation occurred on the surface.

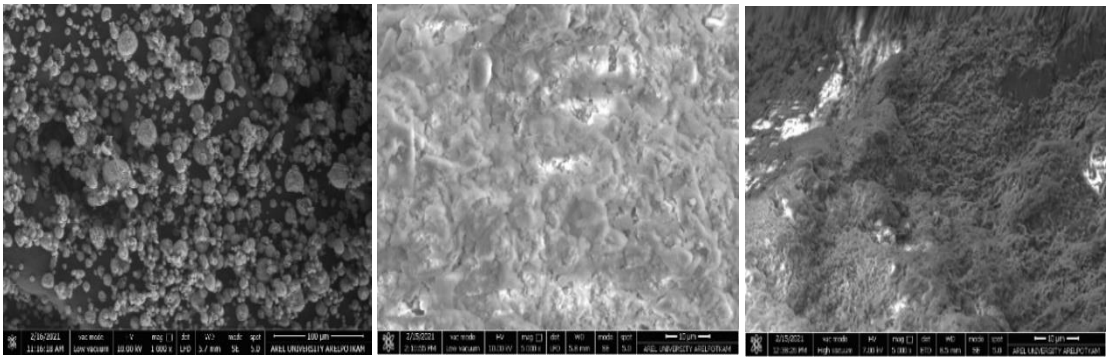

Figure 4.5 : The SEM image of a) nano-clay b) PAN grafted onto nano-clay c) Al sorbed PAN grafted nano-clay.

Analysis of the Aluminum adsorbed sorbent was also performed by EDX analysis. In the structure of the sorbent from the Figure 4.6, there is Si originating from the clay, O, as well as C, N atoms from PAN and Al due to adsorption.

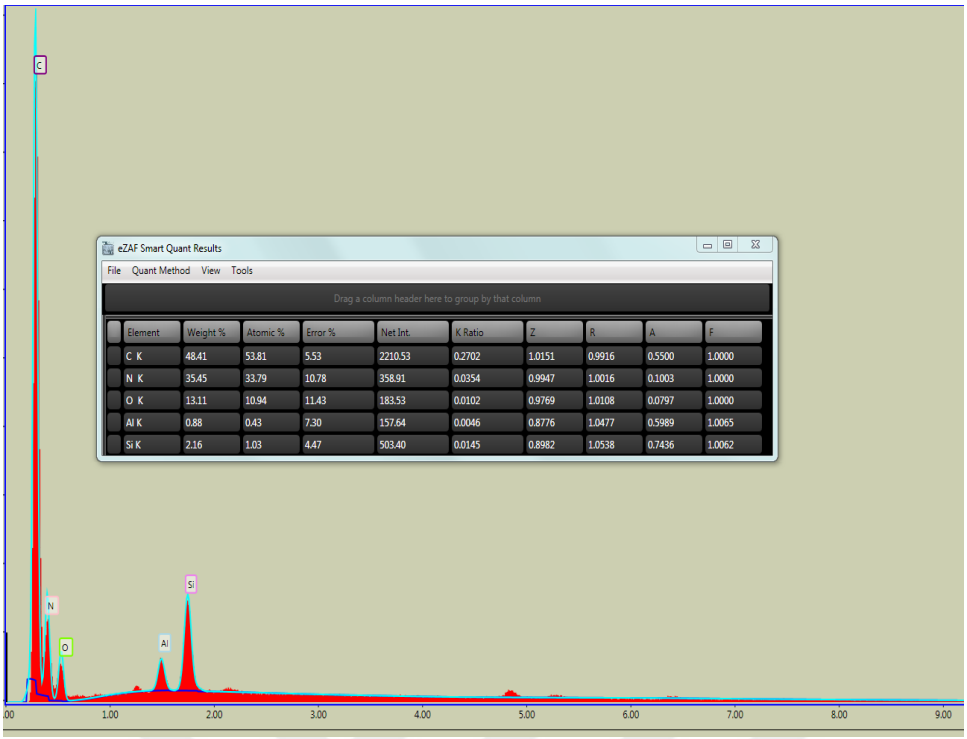

Figure 4.6 : EDX diagram of Aluminum adsorbed sorbent.

4.6 Thermal Characterization of the Sorbent

Thermal degradation experiments were carried out in Shimadzu TA-60WS, Thermogravimetric Analyzer (Kyoto, Japan). The weight loss of samples were measured with a 10 ^{o}C min^{1-} heating rate under flowing air up to 750 ^{o}C.

TG profiles of nano-clay, PAN grafted nanoclay and Aluminum adsorbed PAN grafted nano-clay are shown in Figure 4.7. The similar thermal degradation profiles were observed for PAN grafted nano-clay and Aluminum adsorbed PAN grafted nano-clay. However, incorporation of Al^{3+} to the polymer backbone decreases slightly the degradation temperature of PAN and increased the weight loss amount.

It was concluded that the total weight loss of both samples was measured as 87% in the range of 30-750 °C, but the weight losses in the degradation steps differed. In the first step, weight loss of PKG was measured 29 % between 30-330 °C, in the last step, 58 % weight loss was calculated between 330-545 °C.

In addition, the nanocomposite (Aluminum adsorbed PAN grafted nano-clay) containing Al^{3+} had 3 steps of weight loss. In the first step, 20 % weight loss occurred between about 30 and 130 ^{o}C was due to the dehydration. The second weight loss in the 130-300 °C range was 19 % due to the relase of anions and small fragments into

volatile product. In the last step, 49 % weight loss was occurred due to the polymer originating from the dissociation between 300-530 °C.

According to the results, the thermal stability of the PKG-Al is higher than that of PKG. This is attributed to the presence of Al^{3+} particles in the polymeric structure.

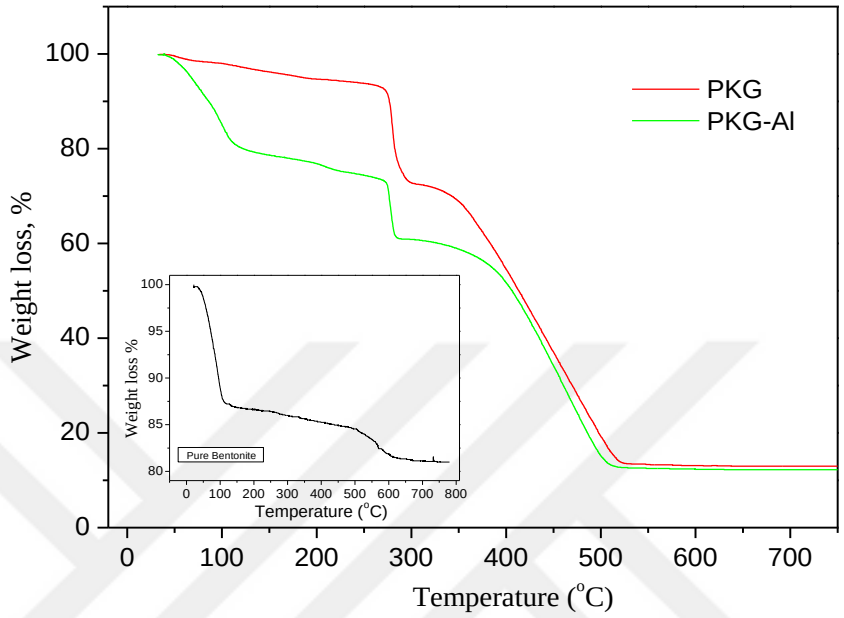

Figure 4.7 : Thermogravimetric analysis of PAN grafted nano-clay and Al adsorbed PAN grafted nano-clay.

4.7 Structural Characterization of the Sorbent

Powder X-ray diffractions of samples were obtained using a Rigaku D/Max-2200/PC diffractometer with the CuKα (λ=1.540) radiation. Samples were scanned from 10 to 90º at a rate of 2°/min.

Figure 4.8 shows the XRD patterns of PKG, PKGAl and nano-clay. Some characteristic peaks at 2θ degree were observed. These are 17.2°, 19.86°, 28.65°, 35.81°, 54.45°, 61.89°, and 73.60° for PAN powders. The characteristic peak observed at 2θ at 19.99º belongs to the pure nano-clay structure. It can be seen that this peak gradually shifts to lower angle with grafting PAN and adsorbing Al^{3+} to nano-clay. According to the Bragg's law, the decrease in 2θ values indicates the increment of the distance between crystal phase.

In Figure 4.8, the XRD patterns of PKG, PKGAl present similar profiles. XRD peak of Al^{3+} structure did not appear because of less Al^{3+} nanoparticle amount in polymeric matrix.

It is noted that the polymeric structure entered between the clay layers and the clay layers were opened also entered the lattice structure of the clay and the crystal size decreased. As a result, nanocomposite materials exhibit low crystallinity and small crystallite size due to interactions between PAN and Al^{3+}.

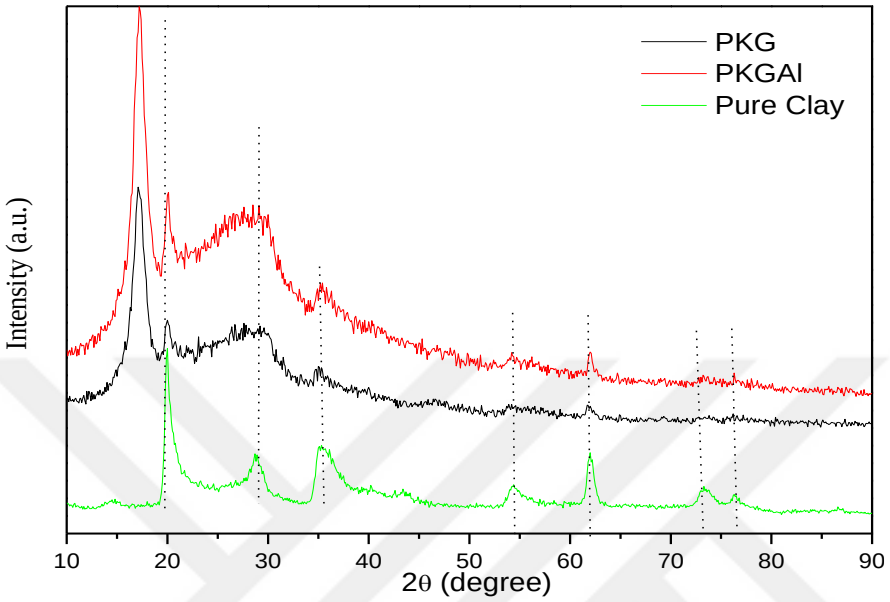

Figure 4.8 : XRD patterns of nano-clay, PAN grafted nano-clay, and Al adsorbed PAN grafted nano-clay.

4.8 Aluminum Sorption Kinetics of the Sorbent

Batch sorption kinetics of the sorbent were investigated highly diluted Aluminum solutions (2 ppm) and depending on temperature. According to the concentration–time plot in Figure 4.9 shows that within about 60 min of contact time, Aluminum sorption reaches maximum value and increasing temperature sorption capacity of the sorbent increasing.

In this study, pseudo first-order and pseudo second-order kinetic models were used to analysis Aluminum sorption kinetics of the sorbent.

The pseudo first-order kinetic model was given with equation 4.3:

$$\mathbf{ln(q_e - q_t) = lnq_e - k_1 t} \qquad (4.3)$$

where q_e and q_t are amount of adsorption ($mg.g^{-1}$) at equilibrium and time t, respectively. The amount of Al adsorbed (q_e) was calculated using the following equation 4.4:

$$\mathbf{q_e = (C_0 - C_e)V/m} \quad (4.4)$$

k_1 (min^{-1}) is the rate constant in the equation. k_1 and q_e, were calculated from slope and intercept of the graph which was plotted $\ln(q_e-q_t)$ versus t [62]. Pseudo first-order equation graph of the sorbent was given in Figure 4.10.

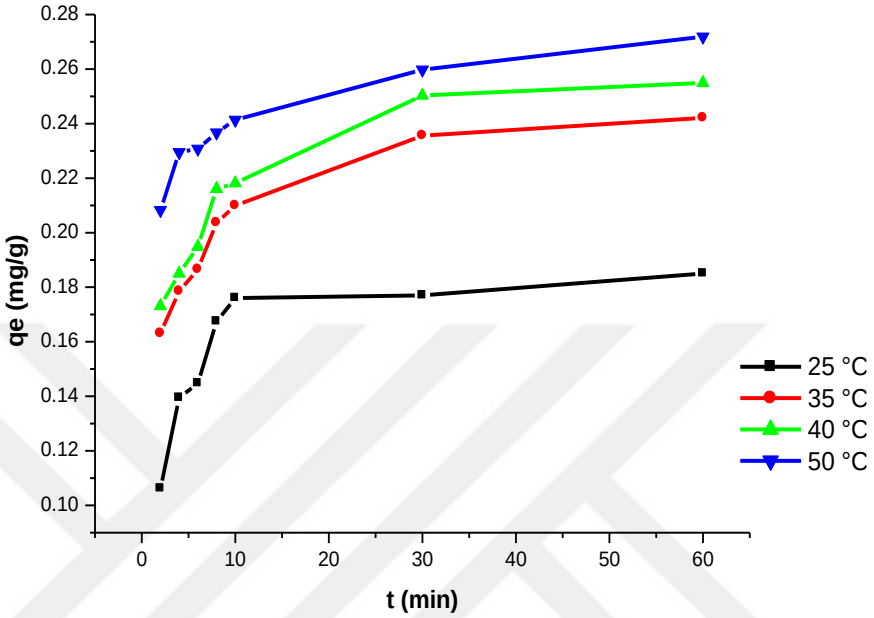

Figure 4.9 : Aluminum sorption kinetics of the sorbent with different temperatures.

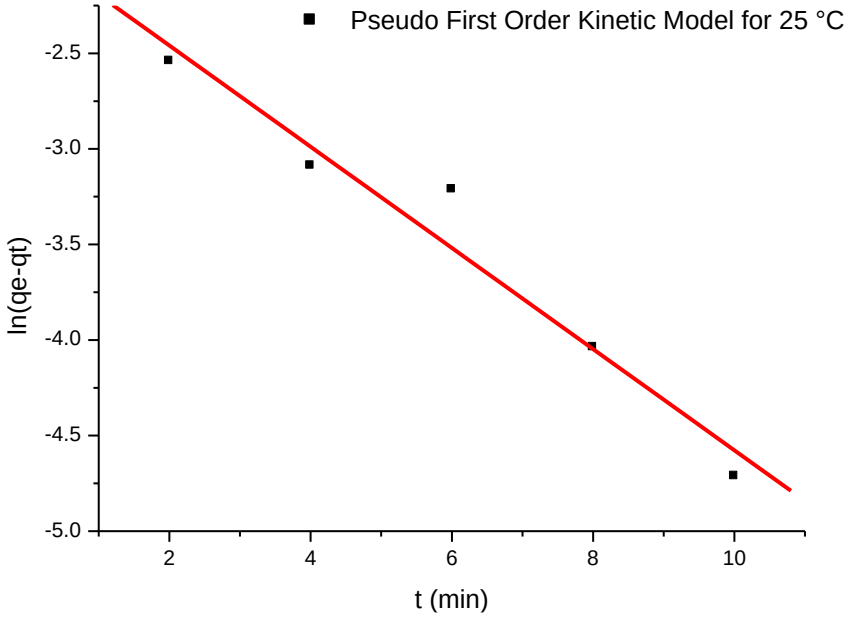

Figure 4.10 : The graph for pseudo first-order kinetic model.

Another important equation which is the pseudo second-order kinetic model is formulated with equation 4.5:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (4.5)$$

Where q_e is the amount of Al adsorbed at equilibrium ($mg.g^{-1}$), and qt is the amount of Al ($mg.g^{-1}$) at any time t. k_2 is the pseudo second-order rate constant in ($g(mg.min)^{-1}$).

q_e and k_2 were calculated from the graph which was plotted $\frac{t}{q_t}$ versus t. The slope and intercept of the graph (Figure 4.11) give q_e and k_2, respectively [62].

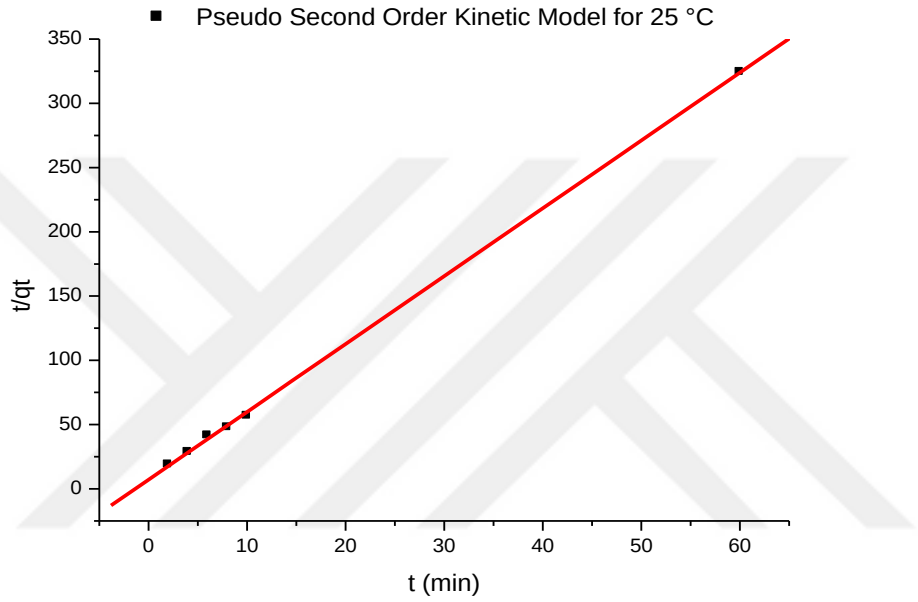

Figure 4.11 : Pseudo second-order kinetics for the adsorption of Al^{3+} onto the sorbent.

Kinetic data of the Al^{3+} sorption onto the PAN grafted nano-clay was given in Table 4.3. If the results are investigated both q_{exp}, q_{theo} and R values, pseudo second-order kinetic model is suitable. Lagergren pseudo second-order model is assumed that the rate limiting step may be chemisorption.

Also, the initial adsorption rate "h" ($h=k_2 q_e^2$) value was found as 0.134 mg/g/min.

Table 4.3 : Kinetic data of the Al^{3+} sorption of the PAN grafted onto nano-clay.

Pseudo First-Order Model				Pseudo Second-Order Model			
q_m(theo) (mg/g)	q_m(exp) (mg/g)	k_1 (min^{-1})	R^2	q_m(theo) (mg/g)	q_m(exp) (mg/g)	k_2 (g/mg.min)	R^2
0.145	0.185	0.265	0.9562	0.189	0.185	3.920	0.9997

4.9 Adsorption Isotherms and Models

Adsorption isotherms indicate some insight into the adsorption mechanism as well as the surface properties and affinities of the sorbents. In this study, Langmuir model (corresponding to monolayer homogeneous sorbent surface) and the Freundlich model (corresponding to heterogeneous sorbent surface) were used. Freundlich model equation was given below (equation 4.6):

$$\ln q_e = \ln K_F + (1/n)\ln C_e \tag{4.6}$$

where qe is adsorption capacity (mg $Al^{3+}.g^{-1}$ sorbent) and Ce is equilibrium Al^{3+} concentration (M) remaining in solution after adsorption process. K_F and n are adsorption capacity ($mg.g^{-1}$) and adsorption intensity, respectively and can be calculated from intercept and slope of graph of lnqe versus lnCe in Figure 4.12.

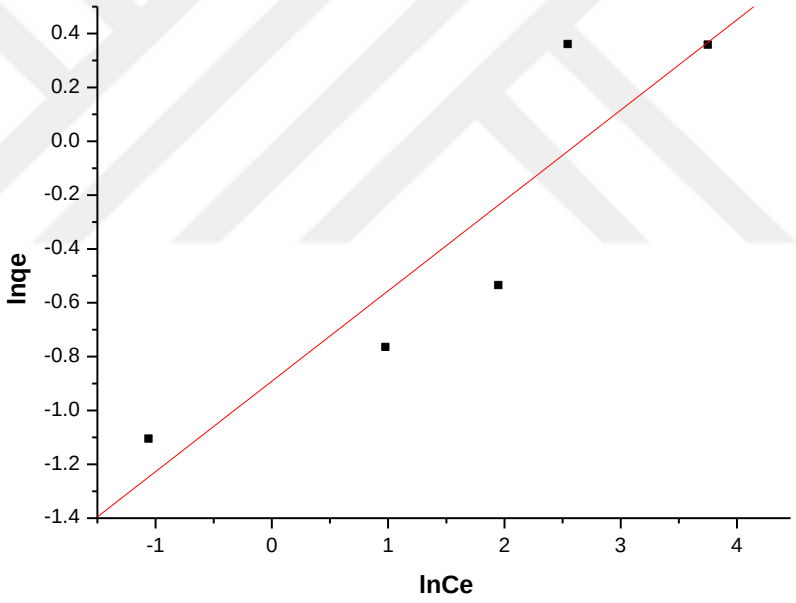

Figure 4.12 : The graph for Freundlich isotherm.

The slope value (1/n) between 0 and 1 is associated with a chemisorption process [84]. In this process, n value was found as 2.979.

Langmuir model explains monolayer adsorption processes on homogeneous surfaces [85]. Langmuir model equation was given below (equation 4.7):

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_m} + \frac{1}{Q_m} C_e \tag{4.7}$$

where q_e is adsorption capacity (mg $Al^{3+}.g^{-1}$ resin) and C_e is equilibrium Al^{3+} concentration (M) remaining in solution after adsorption process. K_L and Q_m are Langmuir constant ($L.mg^{-1}$) and maximum adsorption capacity ($mg.g^{-1}$), respectively and found from intercept and slope of graph of $\frac{C_e}{q_e}$ versus C_e in Figure 4.13 [85].

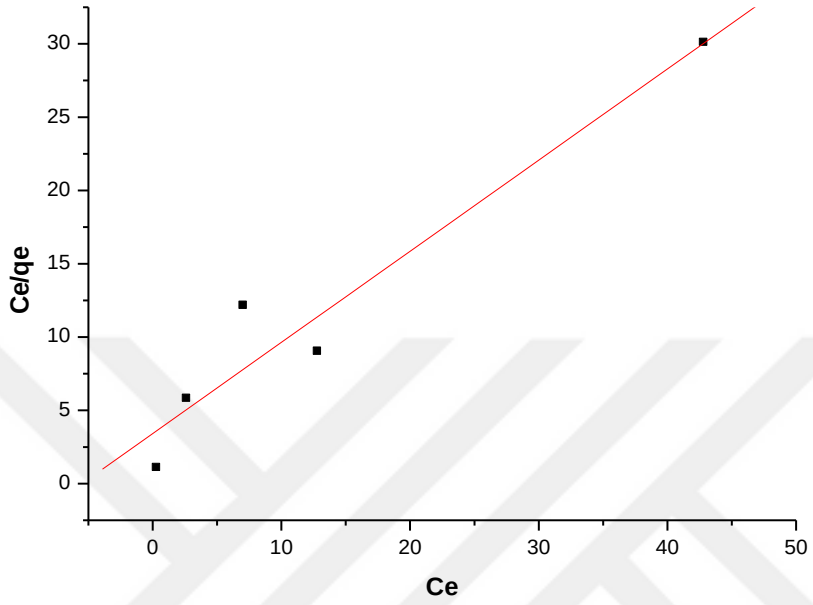

Figure 4.13 : The graph for Langmuir isotherm.

For all of the adsorption isotherm models, constants and correlation coefficients were summarized in Table 4.4.

Table 4.4 : Constants and correlation coefficients of Freundlich and Langmuir isotherm models for Aluminum sorption of the resin.

Freundlich Isotherm Model			Langmuir Isotherm Model		
n	K_F ($mg.g^{-1}$)	R^2	Q_m ($mg.g^{-1}$)	K_L ($L.mmol^{-1}$)	R^2
2.979	0.410	0.8275	1.608	0.182	0.936

If the Table 4.4 was investigated, both Q_m value and R^2 obeys Langmuir isotherm.

5. CONCLUSION

In this study, PAN grafted nano-clay was prepared starting redox polymerization via nano-clay hydroxyl group in the presence of cerium ammonium (IV) nitrate as oxidizing agent and acrylonitrile as monomer at room temperature for 18 h. At the end of the polymerization, grafting degree was calculated as 291.78 %.

Ionic interaction occurs between cyano group and Aluminum ion. This properties was used to remove Aluminum ions from water. After determination of the optimum sorbent quantity, sorption experiments were investigated with depending on different initial concentration and pH. Sorption capacity of the sorbent was found using Langmuir isotherm model as 1.608 mg/g sorbent and this capacity was not change drastically between pH 3 and 6.

Desorption of the Aluminum loaded sorbent was performed using NaOH solution and desorption capacity of the sorbent was found as 1.30 mg/g. And desorbed sorbent was intreracted with NaOH solution again, desorption of the sorbent reaches about 99 %.

Also, kinetic studies and adsorption isotherm calculations were performed. Suitable kinetic model and isotherm model were found as pseudo second-order and Langmuir isotherm model, respectively.

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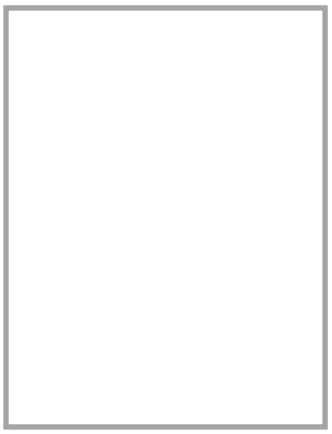
CURRICULUM VITAE



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