



EGE UNIVERSITY



MASTER'S THESIS

**PREPARATION, CHARACTERIZATION AND
SORPTION PERFORMANCE OF SUPPORTED
IONIC LIQUID PHASE (SILP) SYSTEMS**

Merve ARABACI

Supervisor: Assist. Prof. Dr. Nilay GIZLI

Department of Chemical Engineering

Presentation Date: 28.12.2018

Bornova-İZMİR

2018

**EGE UNIVERSITY GRADUATE SCHOOL OF
APPLIED AND NATURAL SCIENCES**

(MASTER OF SCIENCE THESIS)

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MERVE ARABACI tarafından Yüksek Lisans tezi olarak sunulan “Preparation, Characterization and Sorption Performance of Supported Ionic Liquid Phase (SILP) Systems / Destekli İyonik Sıvı Faz(DİSF) Sistemlerinin Hazırlanması, Tanımlanması ve Tutma Başarımlarının İncelenmesi ” başlıklı bu çalışma EÜ Lisansüstü Eğitim ve Öğretim Yönetmeliği ile EÜ Fen Bilimleri Enstitüsü Eğitim ve Öğretim Yönergesi'nin ilgili hükümleri uyarınca tarafımızdan değerlendirilerek savunmaya değer bulunmuş ve 28.12.2018 tarihinde yapılan tez savunma sınavında aday oybirliği/oyçokluğu ile başarılı bulunmuştur.

Jüri Üyeleri:

İmza

Jüri Başkanı : Dr. Öğr. Üyesi Nilay GIZLI

Raportör Üye : Prof. Dr. Mustafa DEMİRCİOĞLU

Üye : Dr. Öğr. Üyesi Ayben Top


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İmzası



Adı-Soyadı

Merve ARABACI

ÖZET**DESTEKLİ İYONİK SIVI FAZ(DİSF) SİSTEMLERİNİN
HAZIRLANMASI, TANIMLANMASI VE TUTMA BAŞARIMLARININ
İNCELENMESİ**

ARABACI, Merve

Yüksek Lisans Tezi, Kimya Mühendisliği Bölümü

Tez Danışmanı: Dr. Öğr. Üyesi Nilay GIZLI

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Bu çalışmanın temel amacı, fiziksel (basit) emdirme ve sol jel olmak üzere iki farklı yöntem kullanılarak hazırlanan destekli iyonik sıvı faz (DİSF) tutucuların hazırlanması ve karakterizasyonun incelenmesidir. Böylece metal iyonlarıyla yüksek ligand yapma ilgisine sahip olduğu bilinen iyonik sıvılar ile geniş yüzey alanına sahip destek malzemelerin adsorpsiyon yeteneklerinin birlikteliğinden doğan sinerjik etkiden yararlanılması hedeflenmiştir. Hazırlanan tutucuların kimyasal, morfolojik ve yüzey alanı tanımlamaları Fourier Dönüşümlü Kızılötesi Spektroskopisi (FT-IR), Tarayıcı Elektron Mikroskopisi (SEM), Brunauer Emmett Teller (BET) analizleri ile incelenirken ısı kararlılıkları Termogravimetrik Analiz (TGA) ile incelenmiştir. Hazırlanan DİSF tutucuların Cr(VI) iyonlarını tutma başarımları bir dizi kesikli ve sürekli denemelerle incelenmiştir. Ayrıca tutucuların metal tutuma süreçlerindeki termodinamik ve kinetik davranışları ortaya çıkarılarak uygun koşullarda sıyırma ve rejenerasyon (geri kazanım) çalışmaları yapılmıştır.

Çalışma, iki farklı yordam izlenerek hazırlanan tutucuların hazırlama karakterizasyon ve adsorpsiyon başarımlarının değerlendirildiği iki ayrı aşamadan oluşmaktadır. Bölüm A'da, fiziksel (basit) emdirme yöntemi ile hazırlanan tutucuların Cr(VI) iyonu giderimi yaklaşık % 100 bulunmuştur. Denge davranışları ise Langmuir model denklemi ile uygunluk sergilemiştir. Fiziksel (basit) emdirme yöntemi ile modifiye edilmiş taneciklerin dolgu kolon sürekli denemelerinde Cr(VI) iyonu giderimi yüksek salıverme kapasitesi sergilemiştir. Bölüm B'de ise, sol

jel yöntemi ile hazırlanan tutucuların Cr(VI) iyonu giderimi % 99 olarak bulunmuştur. Langmuir denklemi ile maksimum tutma kapasitesi 31.74 mg/g bulunmuş olup, adsorpsiyon sürecinin Langmuir izotermine uyduğu görülmüştür. Kinetik çalışmalar adsorpsiyon sürecinin yalancı ikinci mertebeye uyduğunu göstermektedir. Hesaplanan termodinamik parametreler ise adsorpsiyon sürecinin endotermik ve kendiliğinden doğasını göstermiştir. Aynı zamanda 1 M HNO₃ kullanılarak %100 sıyırma verimliliği elde edilmiştir.

Anahtar sözcükler: İyonik sıvılar, adsorpsiyon, destekli iyonik sıvı faz sistemleri, krom



ABSTRACT**PREPARATION, CHARACTERIZATION AND SORPTION
PERFORMANCE OF SUPPORTED IONIC LIQUID PHASE (SILP)
SYSTEMS**

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The main objective of this study is to investigate the preparation and characterization of supported ionic liquid phase (SILP) materials by using different preparation methods such as simple impregnation and sol–gel method. By using these methods, synergistic effect are aimed due to the combination of high ligand-making ability of ionic liquids with the porous properties of silica based sorbents. Chemical morphological characterization and surface area of the prepared adsorbents are investigated by using Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscope (SEM), Brunauer Emmett Teller (BET) Surface Area analysis. The thermal stability of the adsorbents is also evaluated by Thermogravimetric Analysis (TGA). Potential usage of SILP materials as sorbents is determined by a series of batch and continuous studies. Moreover, Cr(VI) ion sorption performances of the prepared adsorbents are investigated regarding the thermodynamic and kinetic aspects.

Results part has two sections according to the preparation methods of materials. In Section A, physical impregnation method is discussed. The removal percentages of Cr(VI) ions are found as almost 100 % for all adsorbents prepared. Sorption isotherms are fitted with Langmuir equation and they exhibit favorable sorption behavior. The packed bed column mode sorption performances of modified particles exhibit high breakthrough capacity. In Section B, sol gel method is performed. The sorption performances of the modified particles are enriched by

impregnation up to 99 % in the aqueous solution. Sorption of Cr(VI) onto modified particles follow the Langmuir isotherm model with the maximum sorption capacity of 31.74 mg/g. The results of sorption kinetic studies show that the sorption process of Cr(VI) ions followed pseudo second order. The calculated thermodynamic parameters indicate that endothermic and spontaneous nature of the adsorption process under operating conditions. Also, desorption efficiency is achieved 100% using 1 M HNO₃.

Key words: Ionic liquids, adsorption, supported ionic liquid phase (SILP), chromium



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PREFACE

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1. INTRODUCTION

Nowadays, environmental related problems are considered to be one of the most important issues because of the fact that rapid industrialization has extremely played a role to the discharge of toxic heavy metals to aqueous media. Hence, it is necessary to treat the metal contaminated aqueous media prior to its release to the environment.

Chromium, which is classified as a heavy metal, is commonly present in waste waters generated from industries and products such as mining, leather tanning, electroplating, textiles, paint, pigments as well as fertilizers. Chromium can exist in aqueous solution in a wide range of oxidation states from -2 to +6 but it commonly occurs in two oxidation states as hexavalent [Cr(VI)] or trivalent [Cr(III)]. The toxicity of chromium depends on its oxidation states. The hexavalent form is hundred times more toxic to aquatic life when compared to trivalent one (Samani et al., 2010).

According to environmental regulations, heavy metal concentrations of chromium must be checked to ensure the discharge limits stated in environmental directives and confirm whether the water can be reused again in other processes. The Environmental Protection Agency (EPA) has verified a Maximum Contaminant Level (MCL) for chromium (total) in public drinking water systems at 0.1 mg/L. World Health Organization (WHO) has also published a regulation to control chromium levels in drinking water (WHO, 2004).

Therefore, it is crucial to develop new techniques in order to remove heavy metal ions from wastewater.

Different types of methods have been investigated in order to remove heavy metal ions like chromium from wastewater. These methods consist of adsorption, ion exchange, chemical precipitation, membrane filtration, flocculation, flotation, coagulation as well as electrochemical methods. The above mentioned techniques both have advantages and disadvantages. However, when operation simplicity, cost

effectiveness and high efficiency is considered adsorption is the most promising method when compared to others (Aydin et al., 2008).

In general, there exist several factors specifying the efficiency of the adsorption such as the surface area, pore size and distribution as well as the surface chemistry of the adsorbents. Due to their excellent physicochemical properties such as high surface area and porosity, porous materials such as silica, macroporous polymer beads are considered as promising sorbents for heavy metal removal. However, these substances do not lead any sufficient efficiency because of their weak binding properties. As a result, modification of these porous sorbents by incorporation or immobilization of the functional groups is a particular concern in order to enhance the removal efficiency as well as to increase the surface adsorption. When most of the applications are considered, ionic liquids (ILs) can be used a chelating agent because of their unique properties such as non-flammability, high thermal stability and negligible vapor pressure (Gizli and Arabacı, 2016).

The combination of an IL with a solid support has been shown to be a promising system for the separation processes. This new technology, termed supported ionic liquid phase (SILP) systems, combines the benefits of ionic liquids with porous solid supports, lead to materials of low toxicity, which are environmentally friendly and have a wide range of separation applications. These materials are prepared by covalent bonding of an IL to a support surface or simply impregnation of the IL phase. Supports are generally clay minerals, silicates or polymers (Zapp et al., 2011).

In this study, the main goal is to prepare supported ionic liquid phase (SILP) systems in order to remove heavy metals such as chromium Cr(VI) from wastewater, to characterize the prepared materials and to investigate the adsorption performance by batch and continuous studies. In accordance with this purpose, simple impregnation and sol-gel method are performed to prepare adsorbents. Chemical structures of the prepared adsorbents are investigated by using Fourier Transform Infrared Spectroscopy (FT-IR) and morphological characterization is obtained by

Scanning Electron Microscopy (SEM). In addition, the surface pore characterization and thermal behavior of adsorbents are examined by using Brunauer Emmett Teller (BET) Surface Area Analysis and Thermogravimetric Analysis (TGA), respectively. Metal sorption performances of the prepared sorbents are investigated by considering Cr(VI) ion sorption regarding the thermodynamic and kinetic aspects. The effect of various analytical parameters on the sorption of Cr(VI) ions such as pH of the solution, initial metal ion concentration, adsorbent dosage, are studied by a series of batch sorption studies. Moreover, breakthrough behavior of prepared sorbents is examined by packed bed column studies.

1.1 Heavy Metal Removal Technologies

Nowadays, heavy metal pollution has become one of the most critical environmental problems. The treatment of heavy metals is a priority concern because heavy metals are not biodegradable and tend to accumulate in living organisms.

Over the last few decades, various methods for heavy metal removal from wastewater have been inclusively studied. These technologies include adsorption, chemical precipitation, membrane filtration, ion-exchange, coagulation, flotation, flocculation, and electrochemical methods (Zhu and Li, 2015).

However, each method has its advantages and limitations in application and they are often limited by technical and economical issues.

The efficiency of **physical separation** such as gravity concentration, flotation, magnetic separation, electrostatic separation, depends on various characteristics such as particle shape and size distribution, heterogeneity of soil matrix, clay content, moisture content, density between soil matrix and metal contaminants, and hydrophobic properties of particle surface (Smith, 1995). However, the disadvantages of the physical separation include high initial capital cost, operation costs and high maintenance fee.

Chemical precipitation is one of the most common and effective process used in industry, because it is relatively simple and low-cost to operate (Ku and Jung,

2001). Traditionally, chemical precipitation processes mechanism is based on changing in form of materials dissolved in the solution into solid particles. Fine particles are formed and chemical precipitants, flocculation, and coagulants processes are used to increase their particle size to remove them as sludge in the precipitation process. Firstly, the metals precipitate and solids are formed, then these solids can be removed and low metal concentrations can be discharged. Hydroxide treatment technique is most commonly used in precipitation because of the its relative uncomplicatedness, low cost of precipitant, and ease of automatic pH control (Gunatilake, 2015). However, it is not efficient way to treat wastewater with high acid content, and a large quantity of toxic sludge that needs to be treated with chemical stabilization and disposed of properly is produced.

Ion-exchange processes have been broadly used to remove heavy metals from aqueous solutions due to their many advantages, such as high treatment capacity, providing effective removal efficiency, and fast kinetics (Kang et al., 2004). For removal of metal ions from solution, charge selective ion exchanger is used in this process. Ion exchange resins are water-insoluble solid materials which can attach positively or negatively charged ions from an electrolyte solution and set free other ions with the same charges into the solution in an equivalent amount. Strongly acidic resins with sulfonic acid groups ($-\text{SO}_3\text{H}$) and weakly acid resins with carboxylic acid groups ($-\text{COOH}$) are widely used as cation exchangers (Fu and Wang, 2011). This technique has also some limitations because of the matrix of the wastewater with high acid levels and high concentration of heavy metal ions. For this reason pretreatment step is required in the process.

Membrane filtration technologies have great opportunity for their high efficiency, easy operation and space-saving. Depending on the size of the particles, there exist various types of membrane filtration such as electrodialysis, ultrafiltration, reverse osmosis, and nanofiltration.

Ultrafiltration is a membrane system working at low transmembrane pressures for the removal of colloidal and dissolved material. If the pore size of ultrafiltration

membranes are bigger than dissolved metal ions in the solution, these ions would pass easily through the ultrafiltration membranes. Ultrafiltration offerings some benefits such as lower driving force and space saving due to its high packing density. Although there are lots of researches in this topic, it has not extensive usage in the industry yet (Fu and Wang, 2011).

Reverse osmosis is one of the separation processes that remove contaminants from aqueous solution by using pressure in order to push the solution through semipermeable membrane. Semipermeable membrane is used in this process which does not allow the passage of the metals on the other side. The membranes used for reverse osmosis have a barrier layer in the polymer matrix in which most separation occurs. The major weakness of reverse osmosis is the high power consumption as a result of the pumping pressures, and the restoration of the membranes (Gunatilake, 2015).

Nanofiltration is a bridging process between ultrafiltration and reverse osmosis. Nanofiltration process has some advantages such as ease of operation, reliability and it has low energy consumption along with high efficiency of pollutant removal when compared to other separation technologies (Fu and Wang, 2011).

Electrodialysis is another membrane separation technique which ions are transported through an ion exchange membrane, under the effect of an electric potential. According to literature, cell performance increases by temperature and voltage. In addition to this, the increment on flow rate decreases separation percentage which allows the treatment of highly concentrated wastewater with heavy metals and to recover undesirable impurities from water (Gunatilake, 2015).

Adsorption is process that occurs when adsorbate accumulates on the surface of adsorbent and increasing concentration depending on the surface affinity. In adsorption process, properties of adsorption, surface interactions, properties of adsorbents and adsorbate as well as properties of system are important parameters. Considering all surface properties, total surface area affects the adsorption mechanism the most. Adsorption process, which is regarded as one of the most

economically friendly and technically easy method is most frequently studied in order to remove heavy metals from wastewater (Zhu and Li, 2015). In addition to this, adsorption is occasionally reversible which means adsorbents can be regenerated by suitable desorption process.

1.2 Chromium and Chromium Chemistry

Chromium (Cr) is a chemical element in the first transitional metal series of the periodic table and its atomic number is 24. It is in a steely-grey colour and has a high melting point. It is also brittle and resistant to tarnishing. In addition to these, chromium is a hard metal that can achieve high polishing. Chromium metal can not be found in nature, but principally it is produced from the mineral chromite (chrome ore). Its valence states range from -2 to +6 and the most common forms are chromium(0), chromium(III) and chromium(VI). These are generally produced by industrial processes such as steel manufacturing, dyes and pigments, leather tanning, wood preserving, and chrome plating (Hamilton et al., 2018).

Cr(VI) is well known to be highly toxic when compared to Cr(III) form in terms of both acute and chronic exposures. According to literature Cr(VI) is hundred times more toxic than Cr(III) because of its high mobility, solubility and bioavailability (Dhal et al., 2013).

Chromium is one of the most commonly used metals in industrialized world which has many forms and applications. Relative to Cr(III), Cr(VI) is highly soluble and mobile under oxidizing conditions and it is toxic to organisms. Therefore, transformation of Cr(VI) to Cr(III) is one of the most widely used approaches in order to remediate Cr(VI)-contaminated environments. Possible transformation between Cr(VI) and Cr(III) are given in Figure 1.1 (Liu et al., 2018).

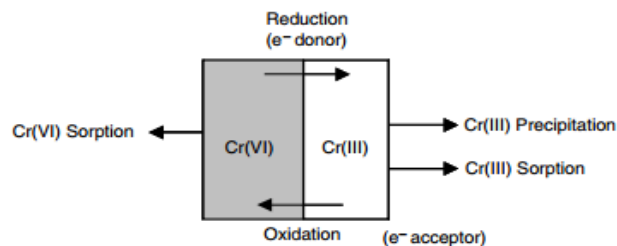


Figure 1.1 Transformation of Cr(VI) and Cr(III).

Dichromate $\text{Cr}_2\text{O}_7^{2-}$, chromate CrO_4^{2-} , chromic acid H_2CrO_4 , and hydrogen chromate HCrO_4^- are most common Cr(VI) species in water and similarly Cr^{3+} , $\text{Cr}(\text{OH})_2^+$, CrO^+ , HCrO_2 and CrO_2^- are formed as Cr(III) species in aqueous solution (Pradhan et al., 2017).

Trivalent chromium Cr(III) is very stable in an acidic environment and if alkaline medium is provided it can oxidize to Cr(VI). Cr(III) compounds can compose a large number of octahedral order complexes. These complexes' colors change according to different crystal field transitions in presence of orderly ligands. The solubility of Cr(III) compounds is less than Cr(VI) in aqueous medium. While oxides of Cr(III) are slightly soluble in water below pH 5.0, hydrated compounds that Cr(III) generated are even less soluble above pH 5.0. At the same time, Cr(VI) usually composes anionic species in water over 60 g/L solubility at various temperature levels. The stability of Cr(III) and Cr(VI) is given in Figure 1.2 as a graphical presentation of the thermodynamic equilibrium states by the help of Pourbaix Diagram. As is known, pH is an important parameter for the redox chemistry of chromium. Cr(VI) is observed as a strong oxidizing agent chromic acid (H_2CrO_4) in strong acidic conditions ($\text{pH} < 1$) and at high Eh. Anionic species HCrO_4^- maintains its stable condition at a high Eh between pH 1.0 and 6.0. As a result of decline in Eh value, equilibrium of HCrO_4^- is observed with Cr(III) from pH 1.0 to 4.0 and from pH 4.0 to 6.0 it exists with $\text{Cr}(\text{OH})_2^+$. Cr(VI) exists as CrO_4^{2-} at above pH 6.0 and with decreasing Eh the equilibria obtain with Cr(III) as CrO^+ (pH 6.0–8.0), HCrO_2 (pH 8.0–9.5) and CrO_2^- (pH 9.5–14.0).

The solubility of Cr(VI) species is very high at all range of pH and that's why we can reduce it to less soluble Cr(III) if we want to remove it from water. Following process could include hydration to solidify the reduced species, instead of direct precipitation of Cr(VI). At adsorption stage the anionic species of Cr(VI) attaches on the polar functional surface in the acidic medium (Pradhan et al., 2017).

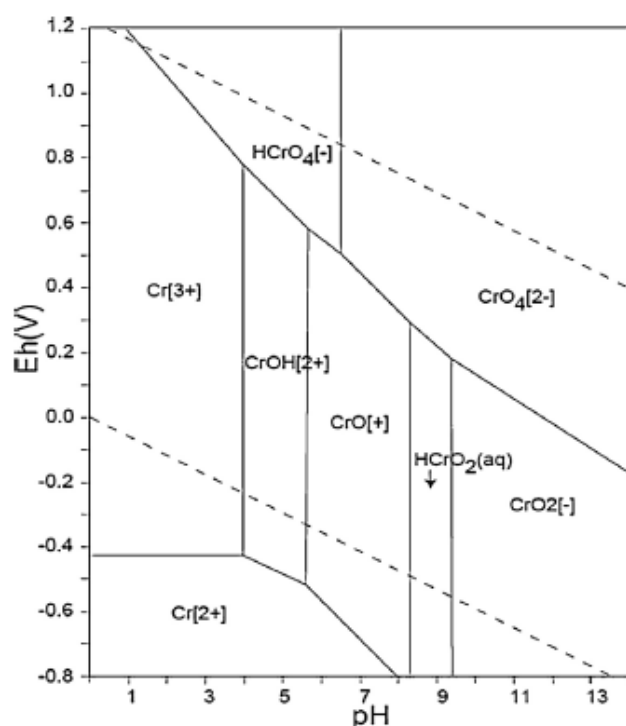


Figure 1.2 Eh-pH phase diagram for chromium (Pourbaix et al., 1966).

Cr(VI) has chemical compatibility and it is one of the frequently used chemicals in numerous industrial applications. This situation naturally causes Cr(VI) pollution. Cr(VI) has toxicity effects on the human body because of that it is important to remove after the processes. This issue is attracting more attention in the environmental research communities' world-wide (Pradhan et al., 2017).

As stated by the World Health Organization (WHO) drinking water guidelines, the maximum allowable limit for total chromium is 0.05 mg L^{-1} (WHO 2004).

Cr(VI) can cause harm by passing through from cell wall. When exposed for a brief period of time beyond the maximum contaminant level, it causes skin and stomach irritation or ulceration. Moreover, long period exposure at levels above maximum contaminant can cause damage to liver, dermatitis, kidney circulation, nerve tissue damage, and even death in large doses (Owlad and Aroua, 2009).

Cr(III) is almost insoluble at neutral pH and less toxic than Cr(VI). Cr(III) is one of the essential elements which is a micronutrient for human body to protect good health and to help in protecting the normal metabolism of glucose, cholesterol, and fat. Human body has several systems to reduce chromium(VI) to chromium(III). These systems provide increment of chromium(III) level via chromium(VI) detoxification (Pradhan et al., 2017).

1.3 Ionic Liquids

Ionic liquids (ILs) have recently classified as “green” and environment friendly solvents that are being potentially investigated as a possible alternative with less environmental effect to conventional volatile organic solvents in reaction and separation processes.

The interest in ionic liquids was initiated because of their advantageous physicochemical properties such as worthy thermal stability, negligible vapor pressure, tunable viscosity and miscibility with water and organic solvents, as well as good extractability, for various organic compounds and metal ions etc. (Liu et al., 2005).

ILs are having low melting point ($<100\text{ }^{\circ}\text{C}$) resulting from the combination of organic cations and variety of anions. Many ionic liquids are present in a liquid state even at room temperature ($25\text{ }^{\circ}\text{C}$). They are mainly consisting of one cation and anion groups. ILs are usually contain an organic cation (e.g., imidazolium, pyridinium, pyrrolidinium, phosphonium or ammonium). The most used ones are asymmetric N,N-dialkylimidazolium cations associated with a variety of anions. 1-n-

butyl-3-methylimidazolium and 1-n-ethyl-3-methylimidazolium are the most investigated structures of this class (Keskin et al., 2007). On the other hand, inorganic anions are usually composed of Cl^- , PF_6^- , BF_4^- , and more currently organic anions, such as trifluoromethylsulfonate $[\text{CF}_3\text{SO}_3]^-$, trifluoroacetate $[\text{CF}_3\text{CO}_2]^-$, bis[(trifluoromethyl)sulfonyl]imide $[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$ (i.e., Tf_2N^-), etc.

Typical structures which combine organic cations with inorganic or organic anions are shown in Figure 1.3 and Figure 1.4.

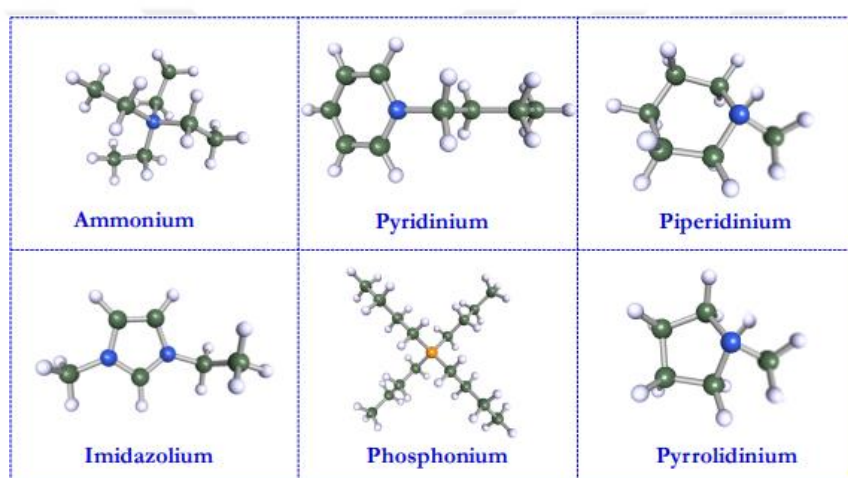


Figure 1.3 Typical structures of common cations of ILs.

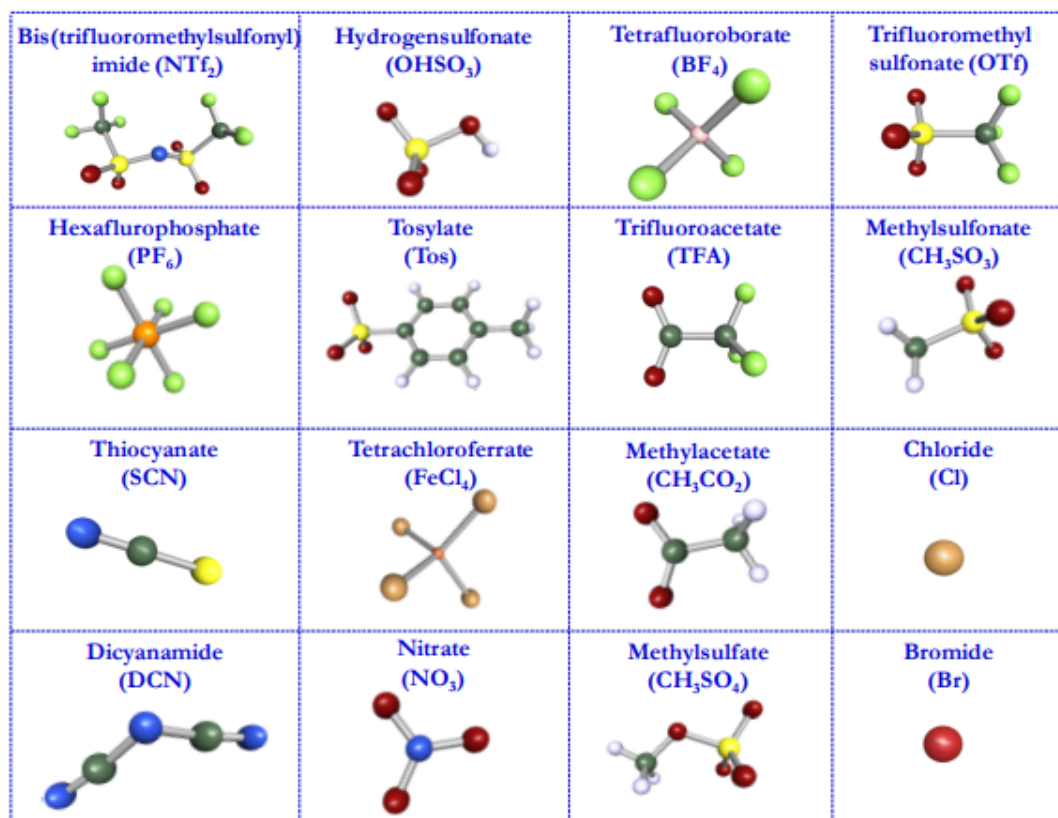


Figure 1.4 Typical structures of common anions of ILs.

The selection of the cation has a strong effect on the properties of the ionic liquid. By changing type of head groups or length of the alkyl chain, physicochemical properties can be altered to fit a particular purpose. For example, melting point and thermal stability are the most remarkable characteristic properties of ionic liquids that can be associated with the structure and composition of ionic liquids. An ionic liquid with a cation with high symmetry has higher melting point when compared to the one with low symmetry. This can be explained by the fact that cations with weak intermolecular interactions and regular distribution of charge in ionic liquids lead to low melting point. In addition to this, many ILs are stable at the temperature over 400°C which provides the opportunity to carry out high temperature reactions at low pressure (Kumar and Khupse, 2010).

Furthermore, viscosity of ionic liquids is considered as crucial. For instance, the alkyl ammonium-based ionic liquids exhibit a higher viscosity than the imidazolium-based ionic liquids with the same anion. Moreover, the viscosity of ionic liquids increases with the length of the alkyl chain on the imidazolium ring, e.g. [EMIM] [NTf₂] < [MMIM] [NTf₂] < [BMIM] [NTf₂] < [HMIM] [NTf₂] < [OMIM] [NTf₂] (Kumar and Khupse, 2010).

1.4 Applications of IL

Nowadays, the variety of industrial and commercial applications of ILs are showing gradually promising viewpoints in the various fields of synthesis catalysis (Hallett and Welton, 2011), materials science (Itoh et al., 2004), electrochemistry (Armand et al., 2009), biochemistry (Jain et al., 2005), pharmacology (Hough et al., 2007) and separation technology (Han and Armstrong, 2007) in both laboratory level and industrial scale. These contributions have shown a great interest in the field of the ILs (Figure 1.5).

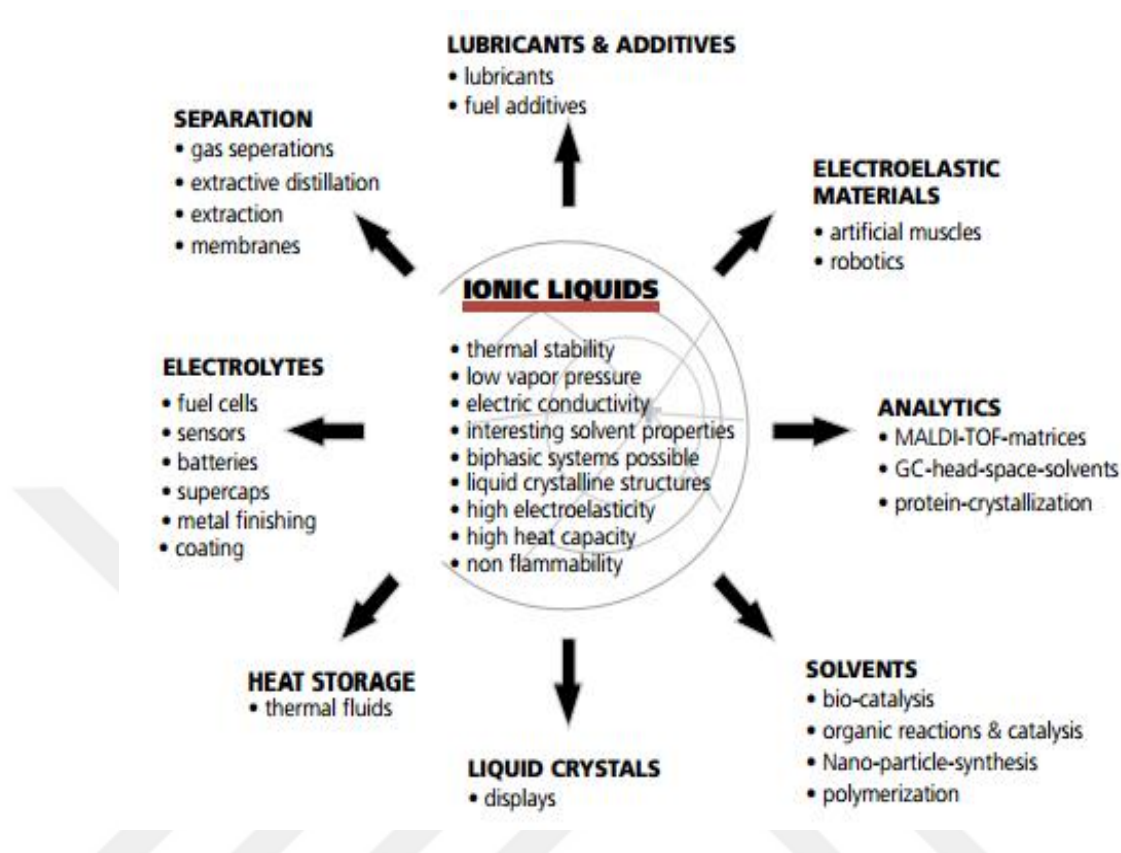


Figure 1.5. Schematic illustration of ILs' advantages and applications (Sigma-Aldrich, 2016).

ILs are innately excellent applicants for industrial applications as alternative to volatile organic solvents. Organic solvents that retain most of the solvent market in the industry have been known for several centuries. Nevertheless, when the properties of organic solvents and ILs which are given in Table 1.1 are compared, it could be expected that industry might be the natural environment for ILs (Fry and Pienta, 1985). Additional properties of ILs are still yet to be discovered and ILs are used better in larger number of industrial processes when compared to organic solvents. ILs stated many academic applications and because of their unique properties ILs are challenging compounds for theoretical and applied studies.

Table 1.1 Comparison of molecular organic solvents and ILs

PROPERTY	ORGANIC SOLVENT	IONIC LIQUIDS
Number of compounds	$>10^3$	$>10^6$
Vapour Pressure	Significant	Negligible
Flammability	Mostly flammable	Mostly inflammable
Polarity	Conventional polarity	Polarity differs
Tunability	Limited Range	Virtually unlimited range
Cost	Generally Cheap	All price classes
Recyclability	Green imperative	Cost and green imperative
Viscosity (cP)	0.2-100	22-40000
Density (g/cm ³)	0.6-1.7	0.8-3.3

ILs are useful solvents for various organic reactions such as Bails-Hillman, Heck Reaction, Diels-Alder, many coupling reactions, and esterification. During the reaction process pressure, temperature and concentrations of reactants are effective parameters. Except above mentioned parameters, it is considered that the viscosity can also play an important role in reaction kinetics. Because of diffusion problems in highly viscous environments, the reactions are also slowing down. This causes retardation in the reaction rates (Kumar and Khupse, 2010).

The first study regarding the usage of room temperature ILs to separate replaced benzene derivatives is made and reported by Rogers and his coworkers (Huddleston and Rogers, 1998).

There are numerous articles about the usage of ILs for electrochemical devices such as lithium ion batteries, super capacitors, and polymer-electrolyte fuel cells enriched dye-sensitized solar cells. ILs serve as electrolyte in an electrochemical devices and they should not be affected easily by electrochemical reduction and oxidation. Non-volatility and prevention of electrolytes from drying during the

operation are two main advantages of using ionic liquids in electrochemical devices (Kumar and Khupse, 2010).

Due to their unique properties, many ILs have been investigated as promising candidate for replacing amines used as solvent in traditional process of CO₂ absorption (Valencia-Morguez et al., 2017). They have a great attraction for the minimization of CO₂/SO₂ emissions (Barros et al., 2018). They are being studied as absorbents in gas separation processes which mainly include CO₂ capture (Han and Row, 2010), (Bara et al., 2009), (Carvalho et al., 2009), (Karadas et al., 2010) and absorption of SO₂ (Hart et al., 2010). CO₂ is absorbed physically by ILs and chemical reactions do not occur. This fact is considered as one of the curicial advantages of using IL for CO₂ adsorption. Another advantage is that, majority of common [C₂mim][X] and their related RTILs are selective during absorption of CO₂ in a mixture of CO₂, N₂ and CH₄. This property is also valid for the available organic solvents used in the industry. Moreover, structure of anion and/or cation can be designed in order to adjust selectivity and solubility of CO₂ in ILs (Bara et al., 2009).

The high solubility of CO₂ in imidazolium-based ionic liquids has been confirmed in many investigations (Blanchard et al., 1999), (Blanchard et al., 2001), (Anthony et al., 2002) (Husson-Borg et al., 2003) (Perez-Salado Kamps et al., 2003) (Cadena et al., 2004).

Moreover, Ren et al. (2018) reported the removal of SO₂ in flue gas by using Task Specific Ionic Liquids. They concluded that Task Specific Ionic Liquids can chemically absorb SO₂ with high capacity and selectivity.

Membrane separation processes are successfully being used in food, pharmaceutical, biotechnology industries as well as in waste water treatment and in various medical applications. In spite of the fact that these processes are considered as efficient, their continuous improvement is essential so that they can catch up the ever changing requirements and needs of the industries, environmental laws and regulations. In the previous years, many researchers have studied the application

possibilities of IL based membranes including the transport and separation of solid materials, liquids and gases. IL membranes have various useful combinations of permeability and selectivity. Many researches are focused on the effort in order to further develop ILs for membrane applications. Through these studies, the ability of lowering the energy intensive and achieving being voluminous of the membrane processes is desired (Petra and Katalin, 2011).

In the hydrometallurgical industry, the most important point is liquid–liquid extraction. Liquid–liquid extraction processes generally use molecular solvents that are flammable, volatile, or toxic. Due to growing concerns about safety and environmental impacts of conventional liquid–liquid extraction processes, the interest in innovative and green extraction processes has increased considerably. It is possible for ILs to replace molecular solvents which are more environmentally friendly because of their properties such as negligible vapor pressure, non-flammability and easy modification. By this way, IL-based extractions can be made less dangerously and can be considered as more nature friendly option for separation technology. ILs draw attention also in media as an important alternative to sustainable separation for ‘green’ liquid–liquid extraction. ILs can be used on metal ions and organic compounds for extraction and separation purposes.

Applications of ILs for the extractions of metal ions can be summarized under two main topics. The first topic, which includes the conventional ILs generally imidazolium type, is ion-type extractants in liquid–liquid extraction processes. The second topic is utilization of ILs as inert diluents to replace volatile organic compounds (VOCs) in the liquid–liquid extraction. The design of ILs composed of non-fluorinated anions and functional cations which directly effects the development of a sustainable IL-based metal ion extraction strategy for any special task such as tricaprylmethylammonium chloride (Aliquat 336, [A336][Cl]). Extractant loss can be minimized successfully by using these ILs for the extraction. Particularly, studies lean over especially on commercial tricaprylmethylammonium chloride ([A336][Cl]) or tricaprylmethylammonium nitrate ([A336][NO₃]). Pure [A336][Cl] or [A336][NO₃] can hold the ion association or anion-exchange mechanism in

extraction process so that organic ligand can be held. Large hydrophobicity, low costs and no cation exchange occurrence are preferable characteristics that make ILs superior to others. On the other hand, [A336][Cl] or [A336][NO₃] are inadequate for the studies, due to their high viscosity when they used as IL extractants in the pure state (Zhu et al., 2015).

1.5 Supported Ionic Liquid Phase (SILP) Materials and Their Applications

ILs have some drawbacks in diffusion-based applications. Considering the application of ionic liquids, the liquid flow and mass transfer rate are considerably limited due to their physical properties such as density and high viscosity. These disadvantages have interested the development of new advanced materials depend on the combination of IL with porous structure of solid supports, approaching the advantages of the separately well-ordered compounds to simply one material (Lemus et al., 2012).

On the other hand, in separation processes, contact area has great importance for effective separation. To increase the contact area of phases, new materials are developed. One of them is supported ionic liquid phase materials. The new approach which is called Supported Ionic Liquid Phase (SILP) technology is to derive ionic liquid containing solid materials that not easily evaporate and prepared through surface modification of porous solids by dispersing a thin film of IL onto it.

Regarding material and surface design, ILs are characterized by a highly restructured uniform liquid structure with unique physicochemical properties by the combination of ions in the material. Therefore, by a suitable choice of the ions contained in the IL material, it is possible to transfer specific properties of the fluid to the surface of a solid material by keeping the fluid to the surface. Hence, the SILP allows tailor made of solid materials, as a result of uniform and well-defined surface structure with significant properties and a controlled chemical reactivity. Most

importantly, the SILP concept constitutes an attractive methodology to circumvent the lack of uniformity of solids in traditional material science (Han and Row, 2010).

Immobilization of ILs on the surfaces of a support by covalent bonding is one of the most common methods. In this method, the IL becomes part of the support material in consequence of losing particular bulk phase properties such as solvation, viscosity, and conductivity (Izquierdo et al., 2011).

The other way is to immobilize IL is direct and the thin film of IL is hold on the surface mainly by physisorption. In this method, the IL is blended with the support and catalyst complex in a low-boiling solvent. Afterwards, the solvent is removed by evaporation (Izquierdo et al., 2011).

These SILP materials offer some benefits compared to classical separation systems as given below,

- A high surface area is obtained by modified support structures
- Mass transport problems prevents by the help of thin film of liquid
- Solvent properties are adjustable such as solubility
- Thermal stability of ILs reaches at the temperature over 200 °C
- Column operations are applied (Hauman et al., 2012).

The SILP system can be shown as schematically in Figure 1.6.

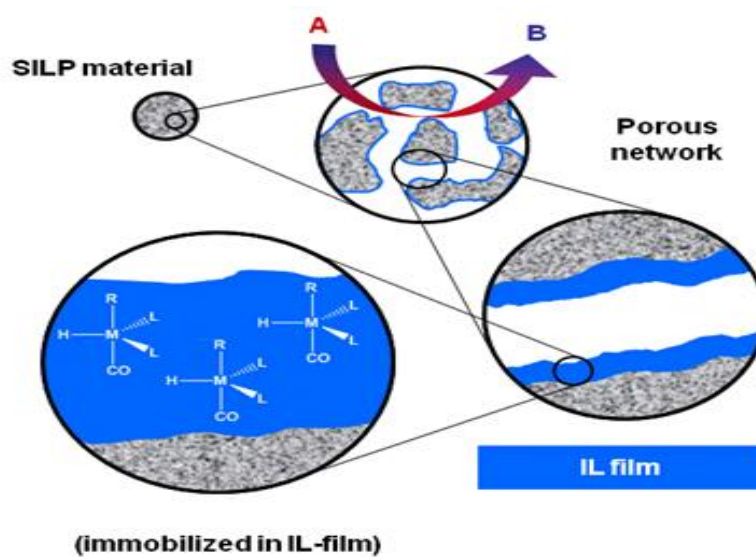


Figure 1.6 Schematic presentation of immobilization of IL into solid support (Mehnert, 2005).

1.5.1 Preparation Methods

In the literature, various methods are developed in order to synthesis SILP materials. The common aim of all methods is to disperse the IL evenly into the porous structure of support material.

Immobilization of ionic liquids can be carried out in many different ways, such as simple impregnation, grafting, polymerization sol-gel method and encapsulation (Lemus et al., 2011).

In this study, ionic liquids are incorporated into solid support to prepare SILP materials by following physical impregnation or sol-gel method.

Physical Impregnation Method

Physical impregnation can be described as the immobilization based on interaction between a solid with a liquid containing the constituents to be released on the surface. Many different processes occur with different rates during impregnation as given below:

- Selectivity of adsorption in the presence of coulomb force, H-bonds or van der Waals forces
- Polymerization/de-polymerization of the species fixed to the surface,
- Partial resolution of the surface of the support
- Ion exchange between the electrolyte solution and the charged surface.

Nature of the liquid phase and the solid surface are important for the efficiency of the operations. pH of the solvent and concentrations of the dissolved substances are effective parameters on the liquid phase. pH plays an important role on ionization process and in many cases, the nature of the ions containing the active elements. Solvent and concentration parameters influence solvation.

The major properties of the solid supports are the porous structure, the nature of functional groups (e.g. the isoelectric point, the number and strength of the acidic and basic centers,), the presence of exchangeable ions and the reactivity (surface dissolution in acidic or basic solution, etc.). There are some general rules that should be considered during the impregnation:

- The properties of the liquid in the pores are different from those measured in the bulk;
- Liquid and solid support equilibrium can take some time and even distribution of attached species inside the pores is not easy to achieved certain level;
- Different types of interaction involves for many deposition process such as coulomb force, van der waals forces , H-bonds (Haber et al., 1995)

Impregnation can be obtained by following various ways;

Impregnation with an excess of solution or by soaking: Solid support and excess liquid are physically attached and then liquid is evaporated or drained. The solid liquid ratio is related to the quantity deposited. Deposition takes several hours or days and is also slow. Large scale reorganization of the surface (loss of surface area, etc.) may take place. However, the method lets the dispersion of the species to be controlled at good level and high dispersions may be achieved. If ion or solid interactions are involved then this method works ideally (Haber et al., 1995).

Dry or pore volume impregnation: In this method, the essential amount of components is presented by the volume equaled to the pore volume of the support. This method preferable for deposition of species which interact highly weakly with the surface and for deposition of quantities exceeding the number of adsorption sites on the surface. When the number of molecules that can adsorb on the surface is smaller, chromatographic effect may be formed, i.e. attachment to the opening of the pores. Redisperison of inside the pores is very slow (Haber et al., 1995).

Wet impregnation: IL is dissolved in a suitable organic solvent or water. The support is added, and the solvent is evaporated. With this method the removal of the metal ions from the aqueous solutions shows high efficiency due to the combination of the properties of the ionic fluid with the advantages of solid support (Vioux et al., 2010).

Sol-gel Method

Sol-gel process is a method which consists of preparation of a solution (sol) and gelation (gel) of the prepared sol with evaporation of the solvent. A sol indicates to dispersion of the solid particles between 0.1 and 1 μm in a liquid media where only the Brownian motions suspend the particles. A gel is a state where both liquids and solids are dispersed in each other, which presents a solid network containing liquid components.

The sol-gel process usually consists of 4 main steps as given in Figure 1.7 below:

1. Formation of a sol
2. Hydrolysis and condensation of molecules
3. Gelation (sol-gel transformation)
4. Ageing and drying

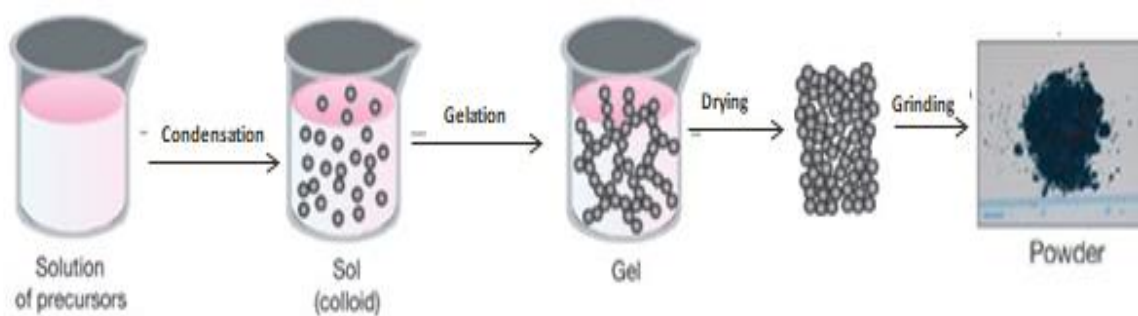


Figure 1.7 Schematic view of sol-gel processing.

The most common precursors are salts, oxides, hydroxides, complexes, alkoxides, acylates and amines. For the silica based sol-gel processes, the precursor materials are generally any alkoxide (Wang and Bierwagen, 2009). Alkoxides are soluble in alcohol and they are hydrolyzed with water under the acidic, basic and neutral conditions. The common alkoxides are tetra ethoxysilane (TEOS) and tetra methoxysilane (TMOS) compounds.

The hydrolysis and condensation reactions commence at numerous sites within the TEOS and H_2O solution as mixing occurs. If adequate interconnected Si-O-Si bonds are structured in region, they give an answer cooperatively as colloidal particles or a sol. With time the colloidal particles are condensed silica species link to form a 3-dimensional network. As a sol transforms a gel, which is called gelation, its viscosity approaches infinity and finally becomes immobile (Zuhal. 2004). During the gelation viscosity rises sharply and the result is an object in the form of a mold. After the sol-gel formation, the solvent phase is taken away from the interconnected pore

network. When hydrolysis is more rapid, polymers are large and more highly cross-linked (Buckley and Greenblatt, 1994).

Two main steps for sol gel process can be summarized as in below.

- Hydrolysis



- Condensation



The sol-gel process depends on several parameters such as pH of the sol, type of alkoxide groups, temperature, amount of solvent and time.

In practice, the reason of evaporation of volatile compounds during the sol-gel reaction is the different complexity which can appear when using alkoxides with low boiling points. Increasing of the chain length of precursor substituent and branching results to the decrease in the hydrolysis rate.

The gelation time and the pore size are affected by the molar ratio of hydrolysis. The role of the material chemistry may not seem very important for after-gelation time. However, there are some interesting aspects especially with respect to homogeneity, purity and porosity of the silica gel under atmospheric conditions, drying comprises the loss of water, alcohol and other volatile components. This leads to gel shrinkage and therewith to high stresses in the structure. This may cause additional random porosity, breaking of the structures and deformation (Rahman and Padavettan, 2011).

The advantages of sol-gel method;

- It allows the oxide composition of both materials which enable the production of both new hybrid organic-inorganic materials.

- The required temperature in all places other than lower concentrations, often close to room temperature. The material can thus be minimized and the risk of thermal degradation can be obtained with high purity and stoichiometry.
- High porosity materials and nanocrystalline materials can be prepared by using this method.
- The speed of hydrolysis, condensation of the pre-starting material by suitable chemical modification of colloidal particle size, pore size, pore surface chemistry and porosity of the final product can be controlled
- By controlling the aging and drying conditions, pore size and mechanical strength can also be controlled.
- Low temperature requirement of the sol-gel process which is often below the crystallization temperature of the oxide material and allows the product to be produced rare amorphous material (Tseng et al., 2010).

The Disadvantages of sol-gel method;

- Pre-starting materials are generally expensive and moisture sensitive. This limits production in large scale for special applications such as optical coatings.
- The process is very time consuming and requires a gradual and careful process of aging and drying.
- In case of a continuous production, the total volume of materials should be processed rapidly (Toygun et al., 2013).

Additionally, ionic liquids are very important organic solvents for sol-gel mechanism. ILs have negligible vapor pressure and they are non-flammable. One of the important properties of ILs is that to have a high stability and this property is improved stability of reactants in IL. Sol-gel systems have the advantages of using ILs as porogens instead of organic molecules. These advantages are the effect of IL on the pore structure and distribution of cation and anion moieties, and the ability to separate ILs from sol-gel systems without leaving residues behind (Shearrow, 2009).

1.6 Literature Survey

Materials, called Supported Ionic Liquid Phase (SILP) systems, which modified by holding ILs on the support can be considered as alternative adsorbent for selective sorption abilities due to providing effective contact area (Kabay et al., 2010, Lemus et al., 2011, Blahusiak and Schibsser, 2014, Lupa et al., 2017). Nanoalumina and nanosilica sorbents are known as the most commonly used adsorbents for solid phase extraction, and adsorption of heavy metal ions (Hua et al., 2012). The hydroxyl groups on the surface of silica and alumina particles are the most important factors for adsorption and extraction processes (Mahmoud et al., 2010). Immobilization of some functional groups of surface modification of alumina and silica nanosorbents and combination of certain functional groups may help to increase the adsorption efficiency of heavy metals (Afkhami et al., 2010, Mahmoud and Al-Bishri 2011, Al-Bishri et al., 2012).

Lemus et al. (2011) reported that immobilization or supporting of ionic liquids can be obtained in many different ways, such as simple impregnation, polymerization, sol–gel method, grafting, encapsulation or pore trapping.

Liang and Peng (2010) examined the removal of the cadmium ions from aqueous solution by using nano silica particles impregnated with various types of ionic liquids. Al-Bishri et al. (2012) studied the removal of lead from the aqueous solution by imidazolium based ionic liquid impregnated nano-silica sorbents.

Liu et al. (2010) investigated adsorption performance of prepared materials by sol gel method using Cyphos IL 104 and Aliquat 336 type ionic liquids. Maximum adsorption capacities were reported as 2.14 and 2.32 mg/g for Cr(III) and 19.31 and 15.29 mg/g for Cr(VI) ,respectively

Wang et al. (2013) obtained a hybrid material by immobilization of 1-methylimidazole [C1] ionic liquid directly onto silica in TEOS medium and they investigate the phenolic component sorption performances.

In this study, Supported Ionic Liquid Phase (SILP) adsorbents were prepared in order to remove Cr (VI) ions from aqueous solutions. This thesis mainly consists of two sections. In Section A, SILPs were prepared by physical impregnation of various types of ionic liquids (commercial and task specific) into solid support materials having various properties such as chemical structure, particle size and surface area.

In Section B, SILPs were prepared by sol gel method using tetraethyl ortosilikat (TEOS) as precursor and using various amount of ionic liquid (tricapryl methyl ammonium chloride [A336][Cl], 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [EMIMTf₂N], tricapryl methyl ammonium nitrate [A336][NO₃]). Chemical, morphological and thermal characterizations of prepared adsorbents were obtained by Fourier Transform Infrared Spectrometer (FTIR), Scanning Electron Microscope (SEM), Brunauer–Emmett–Teller (BET) and Thermal Gravimetric Analysis (TGA) analysis. Cr (VI) ion sorption performances were investigated by batch and column studies considering thermodynamic and kinetic aspects. Sorption performance of support materials were enhanced by incorporation of task specific ionic liquids.

2. EXPERIMENTAL

This section contains materials, methods and procedures followed for the preparation and characterization of adsorbents and their sorption performance evaluation.

2.1. Materials

In this study, three types of ionic liquids such as tricapryl methyl ammonium chloride [A336][Cl] known as Aliquat® 336, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [EMIMTf₂N] and tricapryl methyl ammonium nitrate [A336][NO₃] were used. Although [A336][Cl] and EMIMTf₂N were obtained from Sigma Aldrich, [A336][NO₃] was synthesized with anion metathesis methodology. Chemical structures of ionic liquids are shown in Figure 2.1. Physical properties of ionic liquids used in this study are shown in Table 2.1.

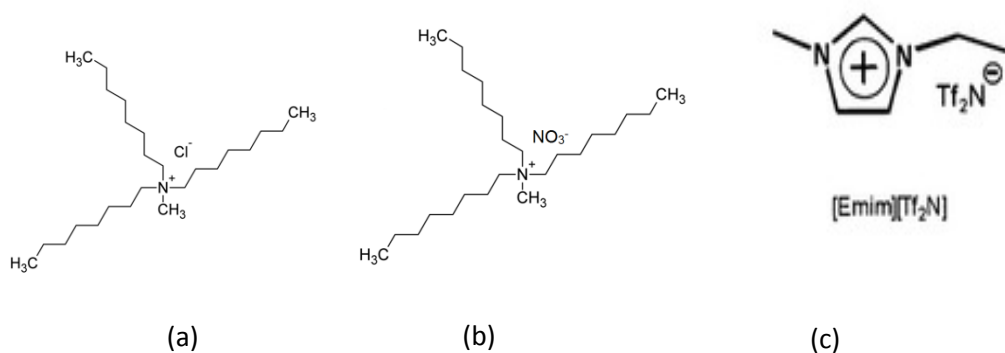


Figure 2.1 Chemical structures of ionic liquids.

a) Aliquat® 336, b) [A336][NO₃], c) [EMIMTf₂N].

Table 2.1 Properties of ionic liquids (Stojanovic et al., 2010).

Properties	EMIM Tf ₂ N	[A336][Cl]	[A336][NO ₃]
Density(g /cm ³) @ 300 K	1.506	0.88	0.9183
Viscosity (cP) @ 300 K	37	1450	201
Conductivity (mS/cm) @	6.66	-	-
Water content by w(%)	-	< 5	8.3

The stock solution of Cr(VI) (1000 mg/ L) was prepared by dissolving an certain amount of K₂Cr₂O₇ in deionized water. The working solutions of different concentrations were prepared by diluting the stock solution. The K₂Cr₂O₇ salt was supplied from Merck, Germany. Aqueous solutions 0.1 M of HCl and 0.1 M of NaOH were used for pH adjustment of solution.

Nano-silica (Aerosil TT600 and Aerosil MOX 80) particles from Evonic Industries and polymeric particles (Amberlite XAD-16) from Fluka, were used as supporting materials. Properties of polymeric and nanoparticles are given in Table 2.2 and Table 2.3 respectively.

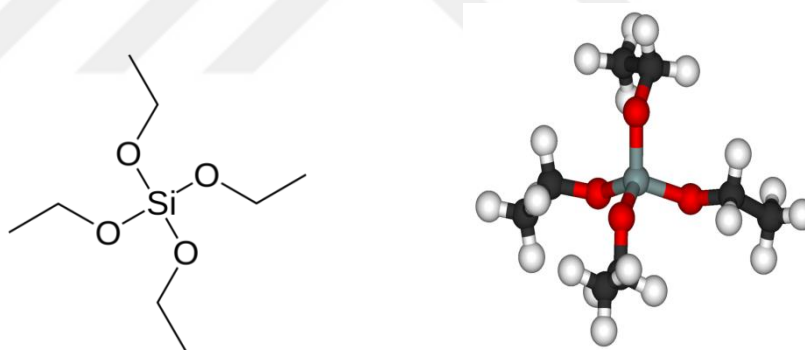
Table 2.2 Properties of polymeric support (Amberlite XAD-16) (Ahmad et al., 2015).

Properties	Value
Density (dry) [g/mL] @ 300 K	1.08
Surface area [m ² /g]	900
Pore Size [Å]	100
Mesh size (wet)	20-60
Pore Volume [mL/g]	1.82

Table 2.3 Properties of nanoparticles (Gizli and Arabacı, 2017).

Properties	Commercial Name	
	Aerosil TT600	Aerosil MOX80
Particle Size [nm]	40	30
Surface Area[m ² /g]	200	80
pH	3.5-4.5	3.5-4.5
Content	SiO ₂ (%100)	SiO ₂ (%99)/Al ₂ O ₃ (%1)

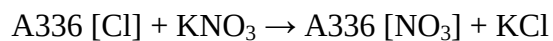
Tetra ethoxy silane (TEOS) was used as a silica precursor. Tetraethyl orthosilicate is the chemical compound with the formula Si(OC₂H₅)₄. It is colorless liquid and insoluble in water, but soluble in ethanol. Chemical structure of TEOS is shown in Figure 2.2.

**Figure 2.2** Chemical structures of TEOS.

2.2 Methods

2.2.1 Ionic liquid synthesis

Task-specific ionic liquid, A336 [NO₃] was prepared by anion metathesis reaction as shown in the following equation below.



To achieve the reaction, commercial Aliquat® 336 ionic liquid solution and 2 M of KNO_3 solution were contacted for 1 hour during vigorous stirring at 25 °C. Phases were then separated by using a separating funnel followed by washing with distilled water. These steps were repeated for 4 times. Completion of the reaction was controlled by checking the Cl^- ion content of the ionic liquid by using AgNO_3 solution.

2.2.2 The ionic liquid impregnated adsorbents (SILP) preparation

In this study, two different incorporation methods were followed as simple impregnation and sol–gel method in order to prepare the SILPs for the removal of Cr (VI) ions.

2.2.2.1 SILP preparation by physical impregnation

SILP adsorbents were prepared by the physical impregnation of the ionic liquid onto polymeric- and silica-based nanoparticle supports through ultrasonification. The solid supports were immersed into 25 mL of ethanol to be swollen in the solvent media. Then, a proper amount of ionic liquid was added and sonicated at a frequency rate of 35 Hertz during 60 minutes. The particles were then left to dry at ambient conditions. The IL content of adsorbents was varied between 0.1 ~ 2.0 g-IL/g-solid support and the prepared SILPs are abbreviated as given in the Table 2.4.

Table 2.4 Abbreviation of prepared SILPs by physical impregnation

ID	Ionic Liquid	Solid Support	Structure of Solid Support
XAD-A	Aliquat 336	XAD-16	SDVB polymer
XAD-TS	[A336] [NO ₃]		
XAD-IL	[EMIMTf ₂ N]		
TT600-A	Aliquat 336	Aerosil TT600	Silica based nano particles
TT600-TS	[A336] [NO ₃]		
TT600-IL	[EMIMTf ₂ N]		
MOX80-A	Aliquat 336	Aerosil MOX 80	
MOX80-TS	[A336] [NO ₃]		
MOX80-IL	[EMIMTf ₂ N]		

2.2.2.2 SILP preparation by sol-gel method

Mesoporous silica particles were synthesized via sol-gel methods using ionic liquids as template. Silica based sorbents were synthesized according to one step process. Firstly, silica precursor, TEOS (5 mL) and EtOH (2.5 mL) were mixed for a while in ultrasonic media. And various amounts of ionic liquids within the range of 0.1-0.7 g were added to the solution and mixed during half an hour at 40 °C. Then, while mixing the solution approximately 2.5 mL of aqueous HCl solution (37 wt%) was added as dropwise to adjust the pH value as 4, and the solution was mixed further for 2 hours. Then, the solution was poured to the moulds and it was left to dry at ambient conditions. It was washed with distilled water and filtered. After drying at ambient temperature, the final product was grinded. The prepared silica adsorbents are abbreviated as given in the Table 2.5.

Table 2.5 Abbreviation of prepared silica adsorbents by sol-gel

ID	Ionic Liquid	Structure of adsorbents
SG-A	Aliquat 336	Functionalized silica based adsorbents
SG-TS	[A336] [NO ₃]	
SG-IL	[EMIMTf ₂ N]	

2.2.3 Characterization

Several methods were used in order to conduct the morphological, thermal and physicochemical characterizations of the material prepared. Fourier Transform Infrared Spectrometer (FTIR-Perkin Elmer Spectra 100) was used to investigate the chemical structure of the modified adsorbents and the functional groups before and after the modification of the nanoparticles with IL. Scanning Electron Microscope (SEM) was used to perform the surface morphology of adsorbents. In addition to this, Energy Dispersive X-ray (EDX) operated in QUANTA 400 F Field Emission spectrometer was used to analyze qualitative element composition. Accelerating voltage of the operating microscope was 20.00 kV. Coating of a gold layer was applied on the particles to make them conductive. Before SEM analysis Brunauer–Emmett–Teller (BET) in Micromeritics Gemini V model was used in order to investigate the pore volume and surface area of silica adsorbents. By using the Micromeritics apparatus, the porous structure of SILP and supports materials were examined with the help of nitrogen adsorption–desorption isotherms at 77 K. Prior to N₂-physisorption study, the samples were degassed for 24 h under flow of dry N₂ at 60 °C. Thermal Gravimetric Analysis (TGA) was carried out in order to investigate thermal behavior of the silica particles under N₂ atmosphere with a heating rate of 5 °C/min, by using Perkin Elmer Diomand TG/DT model.

2.2.4 Adsorption studies

2.2.4.1 Batch sorption studies

The adsorption of Cr(VI) from aqueous solutions onto the modified adsorbents was investigated in a batch process to obtain optimum adsorption parameters such as ionic liquid loading ratio, adsorbent dose, pH and temperature.

Batch sorption studies were carried out by contacting 10 mL of Cr(VI) (50 mg/L) solution with 0.2 g SILP or 0.05 g sol gel adsorbents at 25 °C during 24 h at working pH. The speed of the constant temperature shaking bath (NUVE model ST 30) was kept constant as 150 rpm. Then, sorbents were filtrated by using a filter paper and remained Cr (VI) solutions in the supernatant were determined with the help of Atomic Absorption spectrophotometer (Perkin Elmer Spectra 10+).

For the determination of the effect of pH on Cr (VI) sorption, certain amount of adsorbent was immersed into 10 mL $K_2Cr_2O_7$ solution of 50 mg/L at different pH values within the range of 2-12. The solution pH was adjusted by 0.1 M HCl and 0.1 M NaOH. The mixture was shaken at 25 °C for 24 h. The effect of sorbent doses (0.01-0.3 g for sol gel adsorbents, 0.01-0.35 g for SILP adsorbents into 10 mL of 50 mg/L $K_2Cr_2O_7$) was also examined throughout the batch sorption experiments.

The percentage of Cr(VI) removal (R %) was calculated by using the following expression:

$$R(\%) = \frac{(C_0 - C_e)}{C_0} * 100 \quad (\text{Eq.1})$$

where C_0 and C_e are the initial and equilibrium concentration of metal ion (mg/L), respectively.

To determine the equilibrium behavior of the prepared adsorbents, the adsorption experiments were carried out with the various initial Cr (VI)

concentrations that were ranged from 20–200 mg/L for prepared SILPs by physical impregnation and 5–700 mg/L for prepared adsorbents by sol-gel.

Kinetic studies were performed using 2.5 g of SG-A adsorbent contained in 500 mL of 50 mg/L $K_2Cr_2O_7$ solution at working pH (~5) at a room temperature. The adsorbents was started to the reaction flask at time zero and then a specific amount of solution (~4 mL) was collected at various time intervals in the time from 5 to 240 min.

In the computational part of the study on batch adsorption models, based on the assumption of the pseudo-first order, pseudo-second order and intra particle diffusion and Elovich model mechanism were applied to examine kinetic behavior of prepared adsorbents for the removal of Cr(VI) ions.

Thermodynamic parameters were calculated to confirm the adsorption nature of the study. For these steps, chromium(VI) ion with initial concentration of 50 mg/L was studied in the temperature range of 15-40 °C. The thermodynamic constants, enthalpy change ΔH° , free energy change ΔG° and entropy change ΔS° were calculated to evaluate the thermodynamic feasibility of the system and verify the nature of the adsorption process.

Silica based adsorbents were subjected to metal ion recovery experiments using various concentrations (0.1 to 4 M) of HNO_3 , HCl , $NaOH$ and $NaCl$ solutions. After 24 h of adsorption, the bound metal ions were eluted into 10 mL of each of the elutant for 24 h. After elution, the mixture was filtered and filtrate was measured for metal ion concentration. Desorption efficiency was calculated from the amount of metal ions by following equation:

$$\text{Desorption efficiency} = \frac{\text{Amount of Cr(VI)ions desorbed}}{\text{Amount of Cr(VI)ions adsorbed}} * 100 \quad (\text{Eq.2})$$

Batch elution tests were performed to determine the best conditions for elution of chromium(VI) from the adsorbent.

2.2.4.2 Column sorption studies

Column sorption studies were carried out by passing 0.01 M of Cr(VI) solution through a packed bed column having 0.7 cm inner diameter and filled with 1 mL of adsorbent. The flow rate of the solution has been fixed as 15 bed-volumes per hour (BV/h) by the help of peristaltic pump (Peristaltic PR-2003). Figure 2.3 shows the experimental set up for column wise sorption of prepared adsorbents. A fraction collector was used to obtain effluent fraction having equal volume.

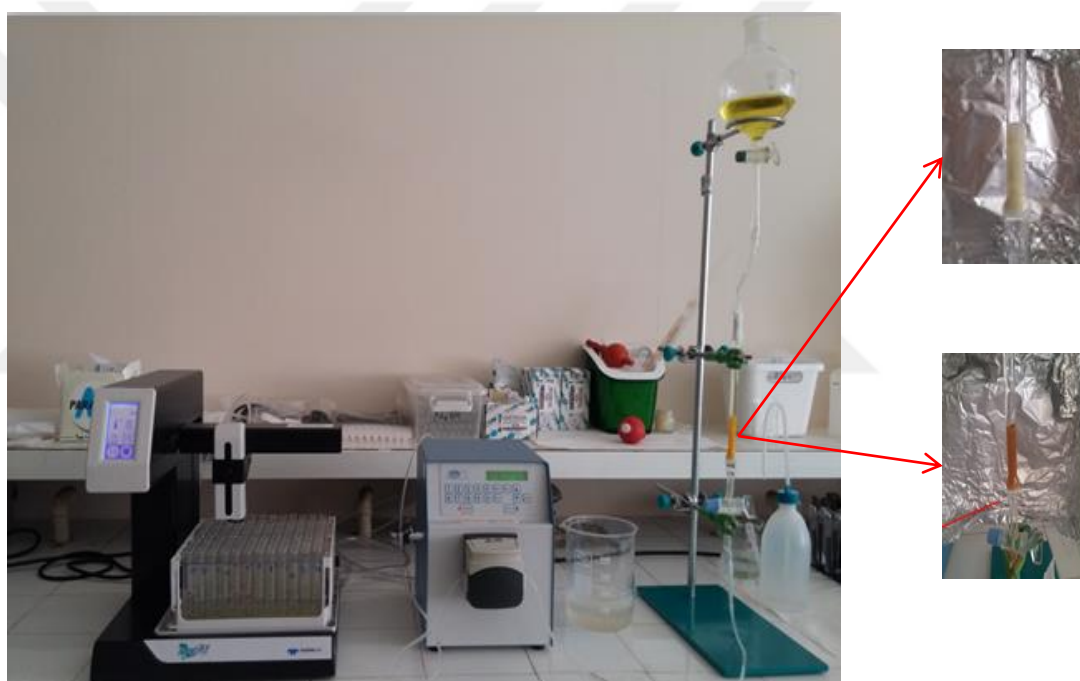


Figure 2.3 Experimental set up for continuous adsorption study

After the sorption capacity of SILPs was completely used they were washed with deionized water and 1 M HNO_3 was passed through the column to elute the chromium ions. The column elution profiles were obtained by analysis of each successive fraction of eluates. To determine the reusability of the adsorbent, a charge–discharge cycle test of SILPs prepared by physical impregnation was done for three times.

3. RESULTS

Results on the removal of Cr (VI) ions are discussed according to the preparation methods:

- **Physical impregnation method**
- **Sol-gel method**

For both of the sections mentioned above, the physicochemical characterization was achieved by Fourier Transform Infrared Spectroscopy (FT-IR) to identify the chemical structure of prepared adsorbents. Surface area and pore volume characteristics of adsorbents were obtained by Brunauer Emmett Teller (BET) analysis. In addition to this, the morphological properties and thermal behavior of adsorbents are examined by using scanning electron microscopy (SEM) and thermogravimetric analysis (TGA) respectively.

Then, Cr(VI) ion sorption performance of SILPs were examined by a series of batch and continuous studies. Kinetic and equilibrium properties of adsorbents were determined. Various kinetic models have been applied to find mass transfer mechanism of the process. Thermodynamic data were also obtained.

The studies conducted can be summarized in the following structure as given below.

SECTION A: Removal of Cr(VI) ions by using SILP prepared by physical impregnation

- Ionic Liquid Synthesis
- SILP preparation by physical impregnation
- Characterization of Adsorbents
 - Physicochemical Characterization (FTIR analysis)
 - Surface Area and Pore Properties (BET Analysis)
 - Morphological Characterization (SEM Analysis)
 - Thermal Behavior Analysis (TGA)
- Sorption Performance of Prepared Adsorbent by Physical Impregnation
 - Batch Sorption Studies
 - Effect of IL Loading Ratio
 - Effect of Solution pH
 - Effect of Sorbent Dose
 - Equilibrium Studies
 - Langmuir isotherm models
 - Freundlich isotherm models
 - Temkin isotherm models
 - Column Sorption Studies

SECTION B: Removal of Cr(VI) ions by using SILP prepared by sol-gel method

- SILP preparation by sol-gel method
- Characterization of Adsorbents
 - Physicochemical Characterization (FTIR analysis)
 - Surface Area and Pore Properties (BET Analysis)
 - Morphological Characterization (SEM Analysis)
 - Thermal Behavior Analysis (TGA)
- Sorption Performance of Prepared Adsorbent by sol-gel
 - Batch Sorption Studies
 - Effect of IL Content
 - Effect of Sorbent Dose
 - Effect of Solution pH
 - Effect of Temperature
 - Evaluation of thermodynamic parameters
 - Equilibrium Studies
 - Langmuir isotherm models
 - Freundlich isotherm models
 - Temkin isotherm models
 - Kinetic studies
 - Pseudo First Order
 - Pseudo Second Order
 - Intra Particle Diffusion
 - Elovich model
 - Infinite solution volume (ISV) model
 - Unreacted core model (UCM)
 - Column Sorption Studies
 - Elution Studies

SECTION A

3.1 Supported Ionic Liquid Phase Materials Prepared by Physical Impregnation Method

This section contains the results of studies conducted with SILPs prepared by physical impregnation.

3.1.1 Ionic liquid synthesis

Ammonium based ionic liquids namely tricaprylmethylammonium nitrate [A336][NO₃] is synthesized with anion metathesis methodology. Physicochemical properties of [A336][NO₃] such as density, viscosity and water content are measured and the values of them are tabulated in Table 3.1.

Table 3.1 Physicochemical properties of [A336][NO₃]⁻

Property	[A336][NO ₃]
Density (cm ³ /g)	0.9183
Viscosity (cp)	201
Water content (%)	8.3

3.1.2 Characterization of adsorbents

The physicochemical and morphological characterizations of SILP materials prepared by physical impregnation have been investigated by Fourier Transform Infrared Spectrometer (FTIR) and Scanning Electron Microscopy (SEM). Thermal stability of the adsorbents was also examined by thermogravimetric analysis (TGA).

FTIR analysis - physicochemical characterization

The FTIR spectra of nanoparticles (TT600 and MOX80) before and after impregnation with EMIMTf₂N ionic liquid are shown in Figure 3.1.

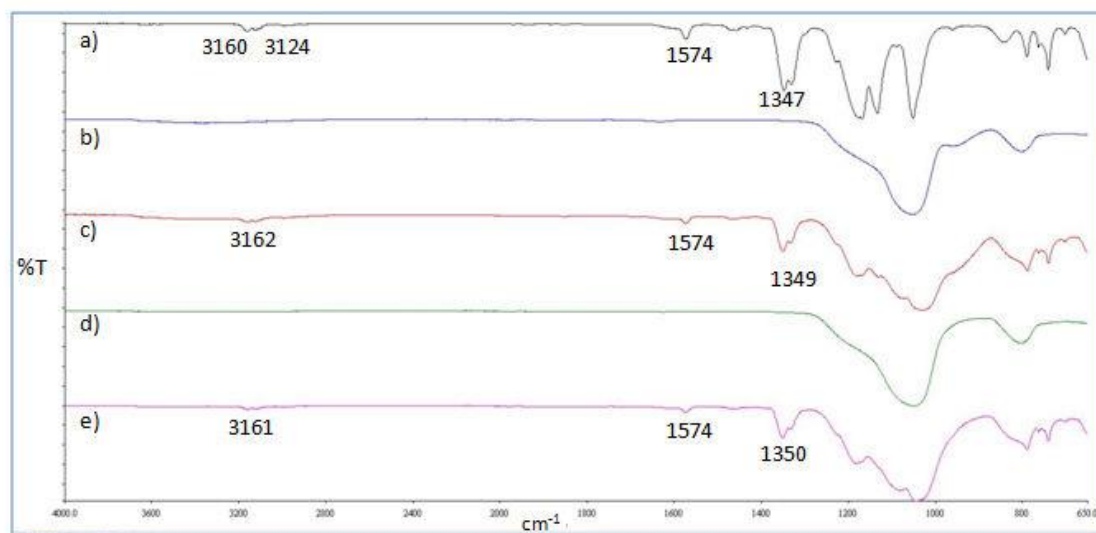


Figure 3.1 FTIR spectrum of adsorbents prepared with [EMIMTf₂N].

a) EMIMTf₂N ionic liquid, b) TT600- before impregnation, c) TT600-after impregnation, d) MOX80-before impregnation, e) MOX80- after impregnation.

The infrared region of the ionic liquid spectrum (Fig 3.1,a), which is between 1400 cm⁻¹ and 1000 cm⁻¹, is mainly dominated and characterized by several peak assignments that are related to the anionic moiety. The characteristic peaks of EMIMTf₂N ionic liquid take places around 3160 cm⁻¹ and 1574cm⁻¹ as can be seen from Figure 3.1 which can be attributed to the C-H and C=C vibrations of the imidazole ring of ionic liquid. In all spectra of the silica nanoparticles, which are given in Figure 3.1 (b, c, d, e), the bands appeared around 1090 cm⁻¹ are attributed to and stretching vibrations of the Si-O-Si groups of the silica backbone. It can also be seen in all spectra of modified nanoparticles that, two new absorption peaks at the wavelengths of 3161 cm⁻¹ and 1574 cm⁻¹ are appeared after treatment of nanoparticles with IL. It is clear that these new adsorption peaks confirm the succesful modification of nanoparticles with ionic liquid.

The FTIR spectra of SDVB particles (XAD-16) before and after impregnation with [A336][NO₃] ionic liquid (are namely p-SILP) shown in Figure 3.2.

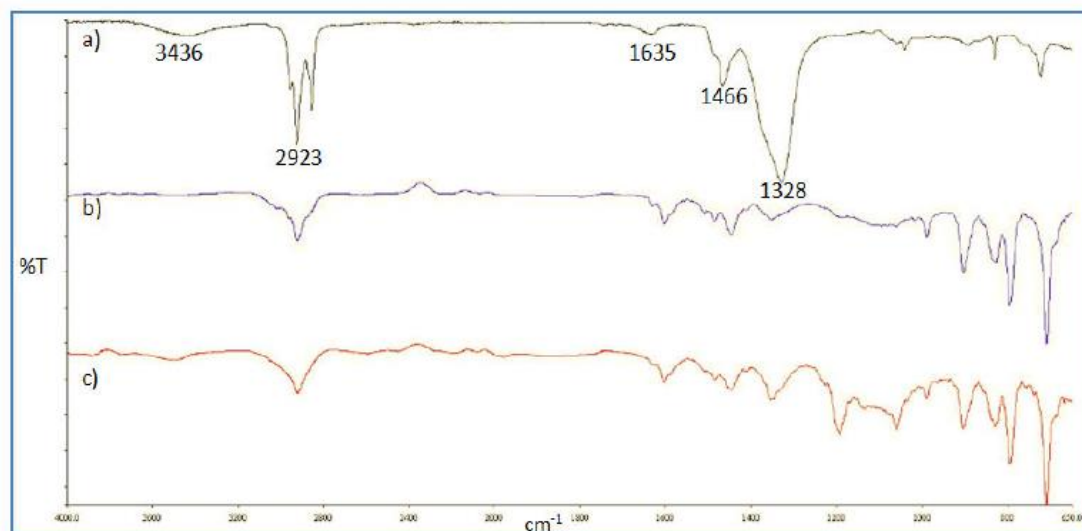


Figure 3.2 FTIR of p-SILP prepared with [A336][NO₃] a) ionic liquid [A336][NO₃], b) XAD-16- before impregnation, c) XAD-TS after impregnation.

In the spectra of [A336][NO₃] given in Figure 3.2 a, peaks located around the wave length of 2923 cm⁻¹ can be attributed to anion group of ionic liquid. A peak at the position of 1466 cm⁻¹ (Figure 3.2 a) which is the characteristic peak of quaternary ammonium moiety of the ionic liquid, becomes pronounced with the impregnation into polymeric supports (Figure 3.2 c).

SEM analysis-morphological characterization

The morphological change of **polymeric support** by modification with [A336][NO₃] can be determined from SEM images of them before and after impregnation presented in Figure 3.3.

It is evident from Figure 3.3 that immobilization of the ionic liquid on the surface of polymeric particles leads to a noticeable characterized change on the morphology. It can be clearly observed that porous structures of the particles are filled with ionic liquid.

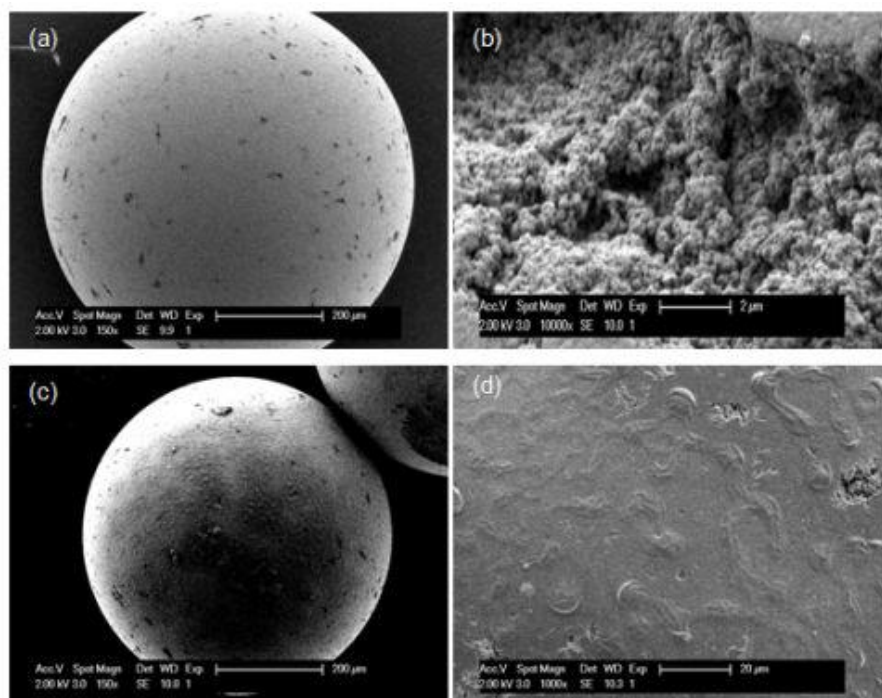


Figure 3.3 SEM images of SILP adsorbent (loading ratio = 1:1 [g-IL: g-support]).
a) before impregnation (X150), b) before impregnation (X10000), c) after impregnation (X150), d)
after impregnation (X1000).

The changes in surface morphology of silica based **nanoparticles** (TT600 and MOX80) by immobilization of IL at various ratios are shown in Figure 3.4 as 2 by 3 matrixes. Impregnation ratio of samples as the amount of IL per g-of support material increases from left to right with specified levels 0.5, 1 and 2.

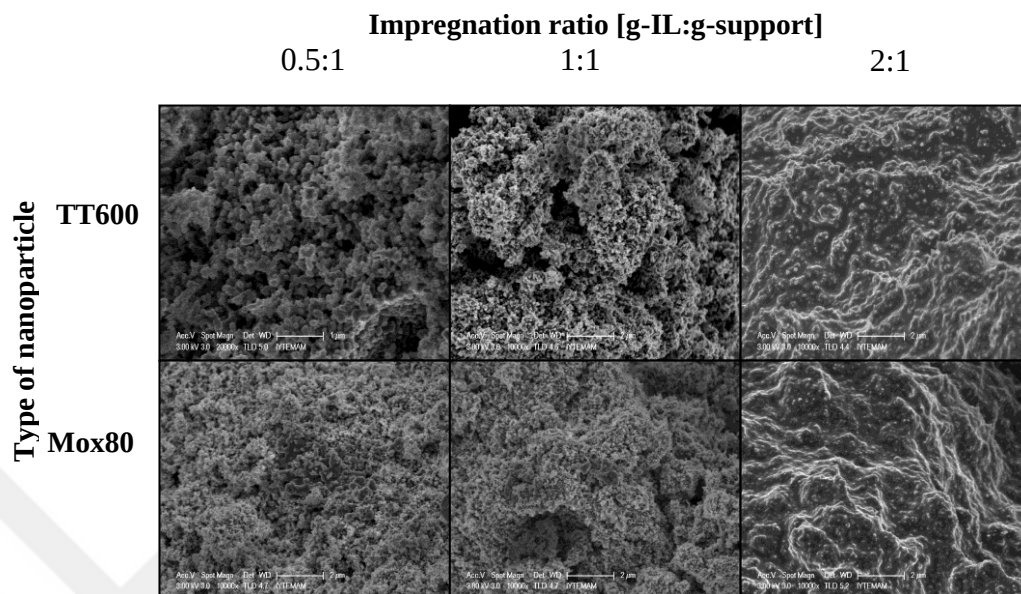


Figure 3.4 SEM images of nanoparticles (TT600 and MOX80) impregnated with ionic liquid at the loading rate of 0.5:1, 1:1, 2:1 (g-IL: g-support).

It is evident from Figure 3.4 that immobilization of IL on the surface of the nano-silica and nano-alumina particles resulted in a pronounced and characterized change on the surface morphology. It is clearly observed that ILs cover the surface of the nanoparticles which lead to a decrease in the surface area by modification.

BET analysis-surface properties

The surface pore characteristics of the solid supports modified by various amount of ILs were examined by BET surface area analysis.

Morphological properties in terms of BET surface area, pore volume and pore size of polymeric and silica based nanoparticles are given in Tables 3.2 and 3.3, respectively.

According to measurements given in Table 3.2 and Table 3.3, there are noticeable decrease in the BET surface area (m^2/g), pore volume (cm^3/g) and pore size values ($\text{\AA}$) after modifying all type of solid supports with the impregnation of

ILs. Surface area of nanoparticles decreased from 200 (m^2/g) to 9.3 (m^2/g) for TT600 and from 80 (m^2/g) to 19.7 (m^2/g) for MOX80. All support materials follow the same trend of drastic decline in their surface area while IL loading ratio increases. From these results it can be concluded that the pores of solid supports are filled with ILs.

Table 3.2 Morphological properties of p-SILP impregnated with TS A336 [NO_3]

Material	Impregnation	S_{BET} [m^2/g]	Pore Volume [cm^3/g]	Pore Size [Å]
p-SILP	Before	950	1.82	100
	After	718.3	1.65	91.95

Table 3.3 Morphological properties of n-SILP impregnated with IL EmimTf2N

Material	Impregnation	S_{BET} [m^2/g]	Pore Volume [cm^3/g]	Pore Size [Å]
TT600	Before	200	0.15	48
	After	9.3	0.013	57.51
Mox80	Before	80	1.6	200
	After	19.7	0.057	114.97

Change in pore size and BET surface area values of p-SILP materials according to the amount of IL loaded can be demonstrated on the Figure 3.5.

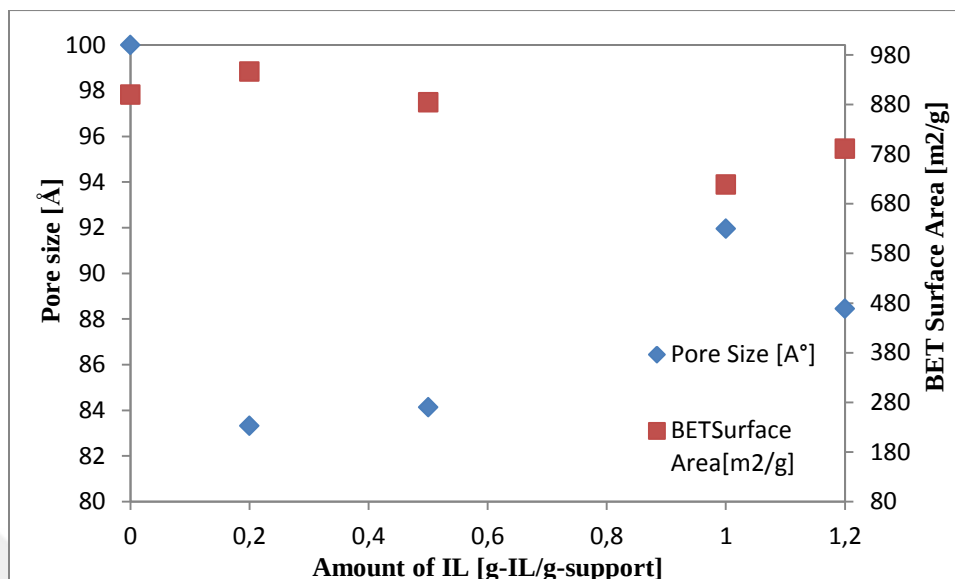


Figure 3.5 Pore size and BET surface area values of p-SILPs.

In Figure 3.5, pore size [Å] decreases from 100 to 83 when the amount of IL is increased from 0 to 0.2 [g IL/g support]. While pore size [Å] increases from 83 to 91.95 when the amount of IL is increased from 0.2 to 1 [g IL/g support]. BET surface area of p- SILP particles decreased from 950 (m²/g) to 718.3 (m²/g) which have the impregnation ratio of 1:1 (g-IL/g-support).

TGA- Thermal behavior analysis

Thermal behaviors of the adsorbents prepared by the impregnation of EMIMTf₂N into the silica based and polymeric solid support are given in Figure 3.6, Figure 3.7 and Figure 3.8.

It is seen that, although the decomposition temperature of pure IL is over the operating temperature, the interaction with the prepared sorbent may lead to decrease in stability. Firstly, the thermal stability of pure IL was examined by TGA within range of 50–600 °C. In Figure 3.6, TGA curve shows that EMIMTf₂N started to decompose at temperature around 400 °C and almost all decomposition reached completion at around 600 °C, as it was stated in literature (Lemus et al., 2011).

Fernandez et. al also reported that common imidazolium-based ILs have very high thermal decomposition temperature (Fernandez, et al., 2007) .

It can be seen from Figure 3.6 and Figure 3.7 that [Emim+Tf2N-] started to decompose at 350 °C and decomposition almost completed at 500 °C. The weight loss of the nanoparticle adsorbents, which have the impregnation ratio of 1:1 (g-IL/g-support), was below 3% at the temperature range of 20-350 °C. However, the nanoparticle supports started to decompose moderately at low temperatures (around 30 °C) and the mass loss of all types of nanoparticles were around 15% at the temperature range of 20-600 °C. SDVB polymeric type solid support (XAD) also started to decompose at the temperatures below 100 °C but decomposition temperature of such type of supports were elevated up to 200 °C by the modification with ILs as seen in Figure 3.8. It can be concluded that the immobilization of ILs may lead to an improvement in the thermal stability of nano-silica and polymeric particles at the temperature range of 20-300 °C.

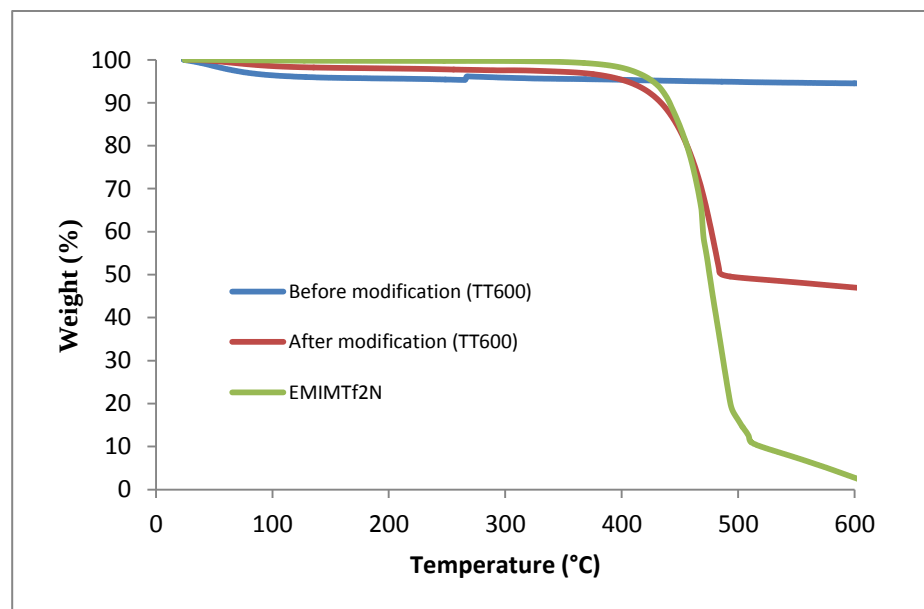


Figure 3.6 Thermal behaviors of silica based nano particles (TT600).

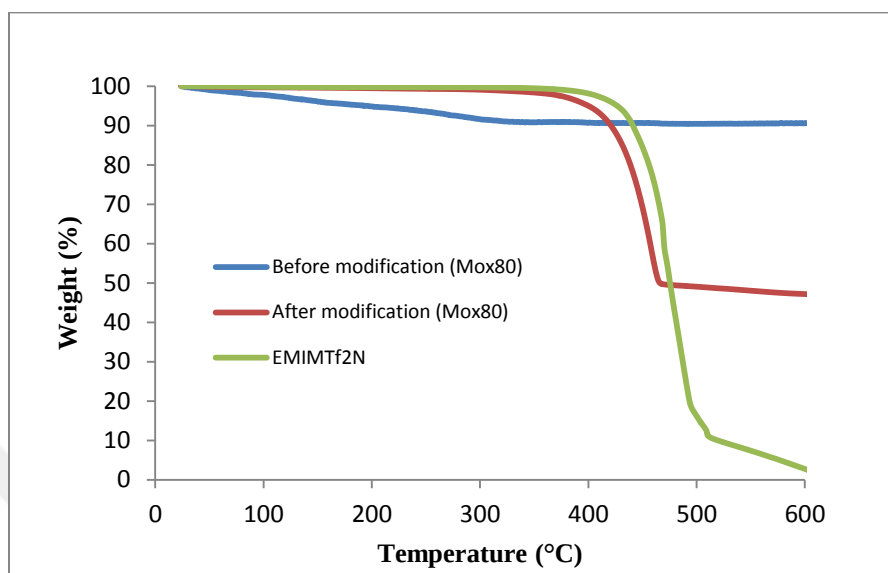


Figure 3.7 Thermal behaviors of silica based nano particles (MOX80).

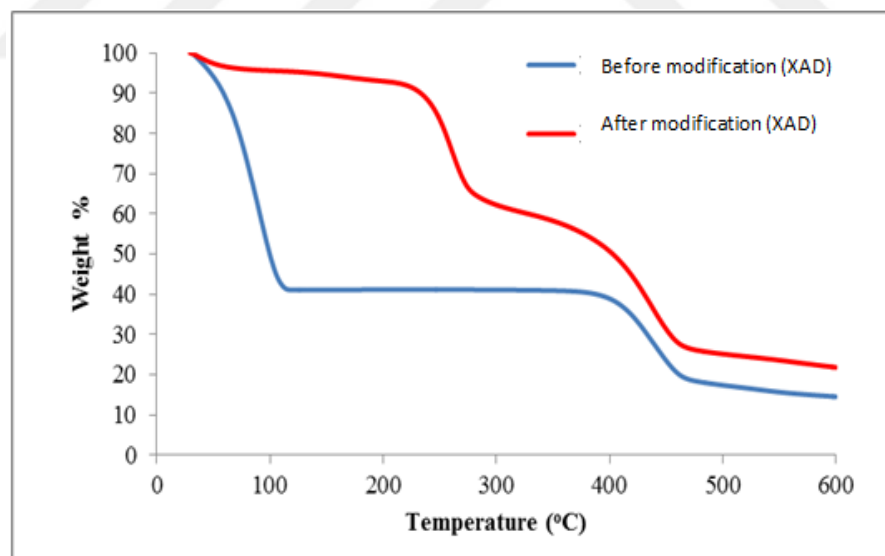


Figure 3.8 Thermal behaviors of polymeric particles (XAD).

3.1.3. Sorption Performance of Prepared Adsorbent by Physical Impregnation

Sorption performances of the prepared adsorbent by physical impregnation were investigated by considering the sorption of Cr(VI) ions.

3.1.3.1. Batch Sorption Studies

A series of batch sorption tests were carried out to obtain the optimum sorption conditions such as adsorbent type, adsorbent dose, pH and contact time for the removal of Cr(VI) ions from aqueous solutions.

The comparative studies for the sorption performance of adsorbents prepared by physical impregnation were carried out by contacting 10 mL of Cr(VI) solution having the concentration of 50 mg/L, with 0.2 g of SILP materials at 25 °C during 24 h.

Adsorption percentage (%) values of bare (unmodified) and ionic liquid confined adsorbents are shown in Figure 3.9.

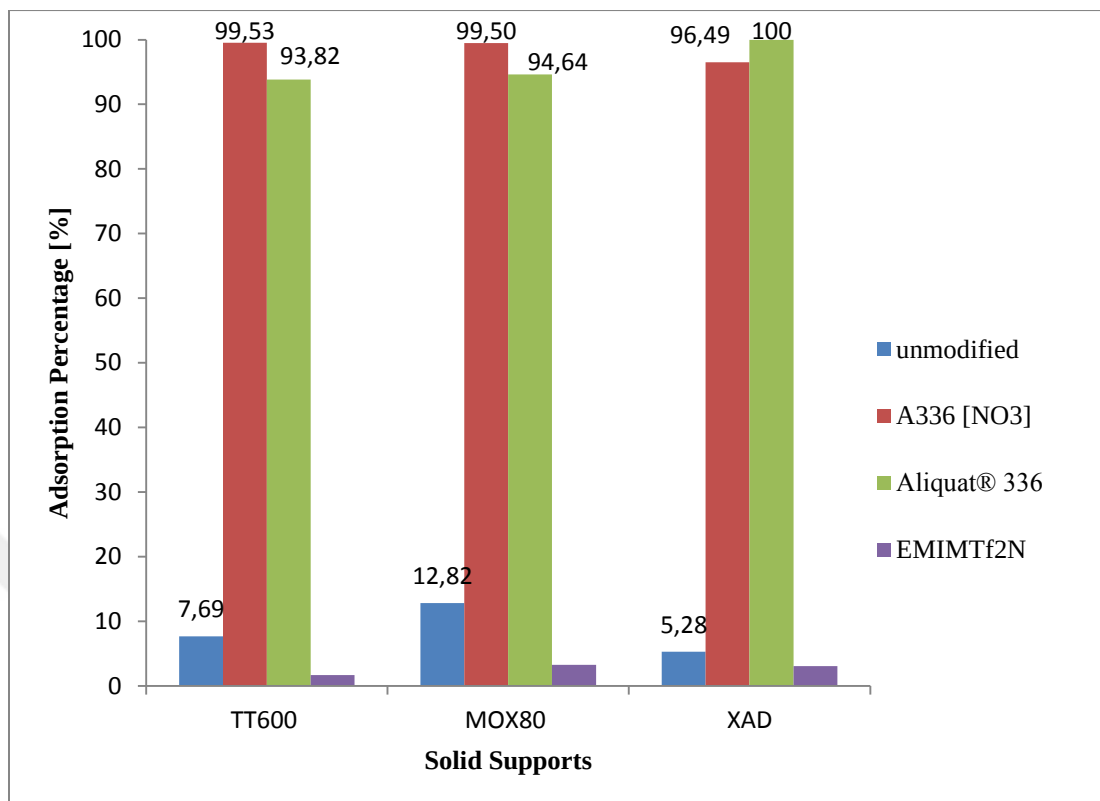


Figure 3.9 Adsorption performance of prepared adsorbents for Cr(VI) removal. [Cr(VI)]₀= 50 mg/L, V= 10 mL, m= 0.2 g, T= 25 °C, t= 24 h].

It is clearly observed from Figure 3.9, that there is a significant increase in the adsorption percentage of all type of support materials after modification with Aliquat® 336 and A336 [NO₃] type ionic liquids. Adsorption percentage of polymeric (XAD) adsorbent was increased from 5.28% to almost 100% after impregnation with Aliquat® 336 and A336 [NO₃]. Similar adsorption performances were also achieved by TT600 and MOX 80 nanoparticles. However, the sorption performances of all type of sorbents containing EMIMTf₂N ionic liquid, dramatically decreased comparing to the others. It can be concluded that Aliquat®336 and A336 [NO₃] type ionic liquids might be attached to the solid support by electrostatic interactions and sorption took place under the effect of anion exchange reaction. Since Cr(VI) exists predominantly in the form of (HCrO₄)⁻ and (Cr₂O₇)²⁻ ions in aqueous phase at working pH value. On the other hand, EMIMTf₂N ionic liquid did not play a role in an ion exchange reaction and repulsion effect was observed for that

working pH range. In consideration of these results, the performance of adsorbent modified with EMIMTf₂N ionic liquids was not investigated for further studies.

Effect of IL Loading Ratio on the Sorption of Cr(VI) Ions

The effect of the amount of ionic liquid (Aliquat® 336 and A336 [NO₃]) loading ratio on the Cr(VI) adsorption percentage was investigated by using SILP containing various amount of IL(g) per solid support (g). The impregnation ratios were selected as 0.2:1, 0.5:1, 0.7:1, 1:1, 1.2:1, and 2:1 (g-IL/gsupport). The effects of IL loading ratio on Cr(VI) removal performance for XAD, TT600, and MOX 80 are shown in Figure 3.10-3.12, respectively.

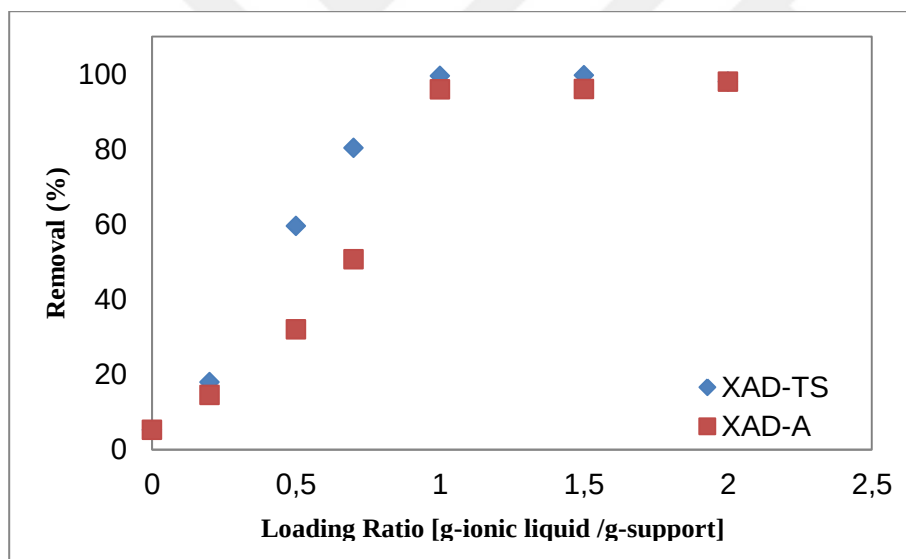


Figure 3.10 Effect of ionic liquid loading ratio on Cr(VI) removal performance of XAD supports. [Cr(VI)]₀ = 50 mg/L, V = 10 mL, m = 0.2 g, T = 25 °C, t = 24 h].

At the given conditions, it can be clearly seen from Figure 3.10 that the increase in the IL loading ratio for both XAD-A and XAD-TS, resulted in the increase in the percentage of adsorption until the loading ratio of 1:1 g-IL/g-support. Adsorption percentages were found nearly 100% and 96% for XAD-A and XAD-TS, respectively.

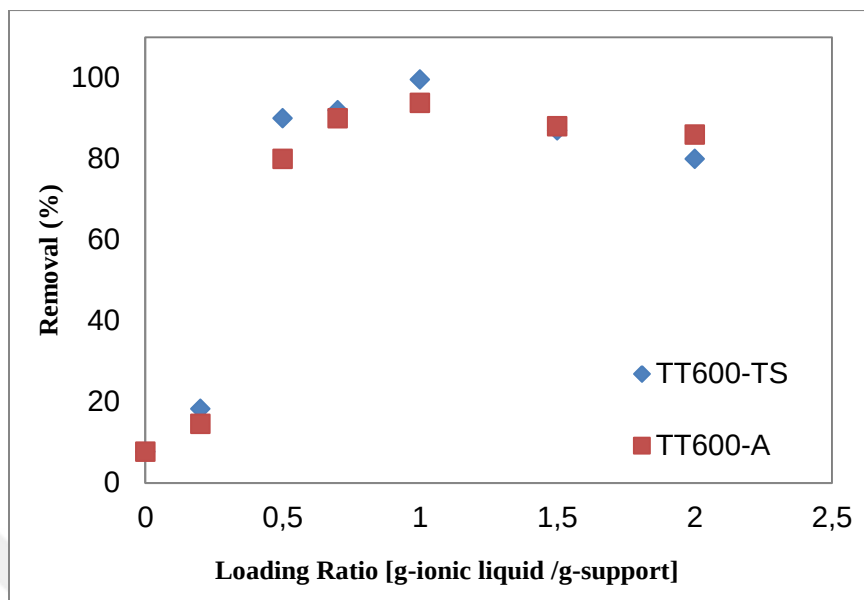


Figure 3.11 Effect of ionic liquid loading ratio on Cr(VI) removal performance of TT600. $[\text{Cr(VI)}]_0 = 50 \text{ mg/L}$, $V = 10 \text{ mL}$, $m = 0.2 \text{ g}$, $T = 25^\circ \text{C}$, $t = 24 \text{ h}$

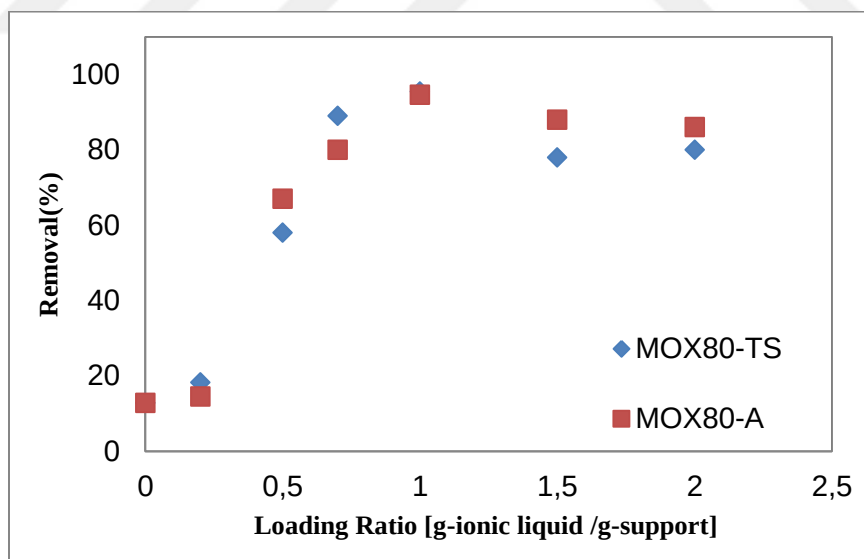


Figure 3.12 Effect of ionic liquid loading ratio on Cr(VI) removal performance of MOX 80. $[\text{Cr(VI)}]_0 = 50 \text{ mg/L}$, $V = 10 \text{ mL}$, $m = 0.2 \text{ g}$, $T = 25^\circ \text{C}$, $t = 24 \text{ h}$

It is clearly seen from Figures 3.11 and 3.12, that up to a certain value (1 g /g support) the adsorption percentage of the adsorbents increased with increasing loading ratios. After this value, it can be said that adsorption yield decreased with the

decrease in the value of surface area because of the occupying the pores of particle with IL. Impregnation with A336[NO₃] type ionic liquids demonstrated the higher achievement compared to commercial ionic liquid for both MOX 80 and TT600. For further studies, IL loading ratio was chosen as 1:1 (g-IL/g-support) for all type of SILPs.

Effect of Solution pH

The solution pH is one of the major parameters to find out the adsorption capacity of SILPs for Cr(VI) ions.

Figure 3.13 shows the sorption performance of silica based adsorbents at the pH range of 2-7.

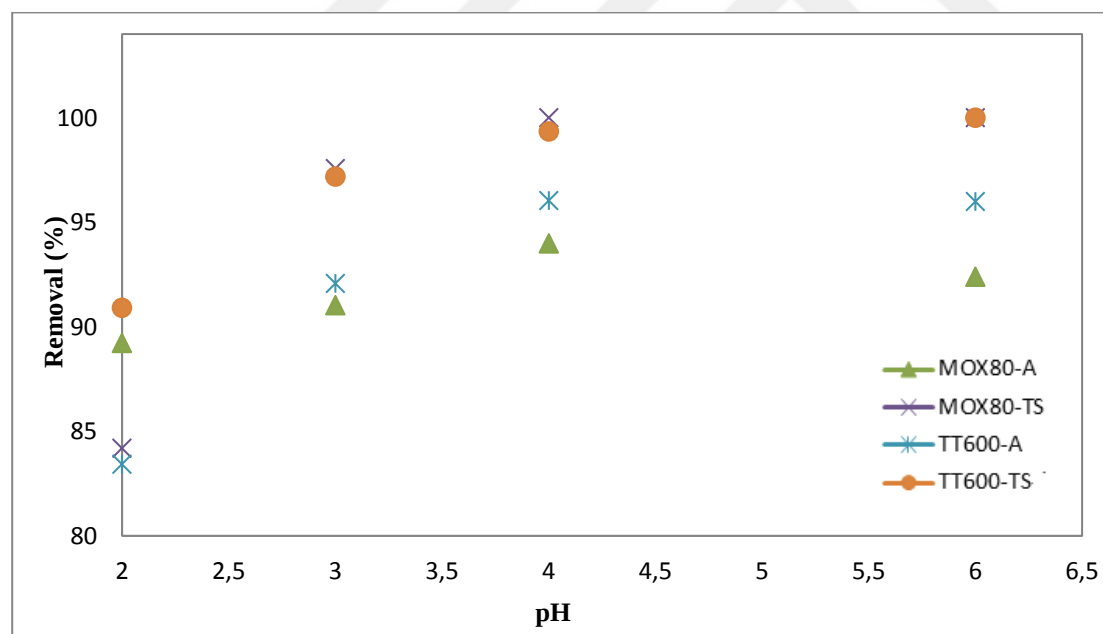


Figure 3.13 Effect of pH on the adsorption of Cr(VI) onto adsorbent (TT600 and MOX80).

[Cr(VI)]₀ = 50 mg/L, V = 10 mL, m = 0.2 g, T = 25 °C, t = 24 h.

In Figure 3.13, it is shown that the removal of Cr(VI) ion increases with increasing pH from 2 to 4. Almost complete removal of Cr(VI) was obtained at pH value of 4. After that value of pH, nearly no further changes in percentage of

adsorption yield is observed. This situation can be explained by the formation of HCrO_4^- ions predominantly, and the reaction with anionic group of ionic liquid by ion exchange reactions in pH values between 2 and 4. Above pH 4 predominantly form of CrO_4^{2-} was formed in the solution.

The effects of pH on the adsorption of Cr(VI) onto polymeric adsorbents are shown in the Figure 3.14.

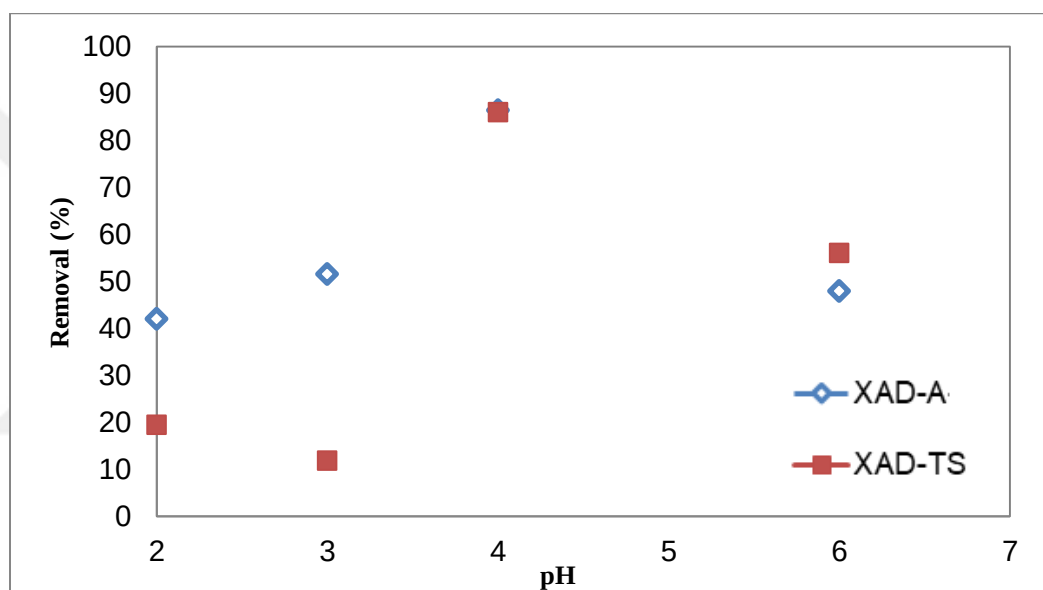


Figure 3.14 Effect of pH on the adsorption of Cr(VI) onto SILP adsorbent.

[Cr(VI)]₀ = 50 mg/L, V = 10 mL, m = 0.2 g, T = 25 °C, t = 24 h].

In Figure 3.14. it can be clearly seen that removal of Cr(VI) ions increases with increasing pH between 2 and 4. After pH 4, a sudden decrease was observed in the percentage removal. According to Figures 3.13 and 3.14, the optimum pH value was specified as 4.

Determination of the surface charge properties of adsorbents

It is known that pH has importance in sorption since pH effects chemical speciation of the metal in the solution and also on the ionization of chemically active

sides on the sorbents. Thus the determination of the point of zero charge of sorbent plays a crucial role in the sorption processes.

Point of zero charge (pzc) determines the surface charge of the sorbent at a given pH and its knowledge informs about the possible electrostatic interactions between sorbent and metal components. The charge of the positive surface sites is equal to that of the negative ones at pH_{pzc} . While at pHs lower than pH_{pzc} , sorbent surface is positively charged and may interact with negative species. At solution pHs higher than pH_{pzc} , sorbent surface is negatively charged and may interact with metal positive species (Fiol and Villaescusa, 2009).

To determine the point of zero charge values of sorbent, 1 g of prepared adsorbents were put into contact with 0.03 M of KNO_3 solution adjusted at various pH values ranging from 2 to 12 by using 0.01M NaOH and 0.1 M HCl. The solutions were shaken for 24 h at 250 rpm at temperature of 25 °C until an equilibrium pH value was obtained. Then pH_{pzc} is the pH at that a plateau is achieved when plotting pH final versus pH initial values. Calculated pH_{pzc} values of prepared adsorbents by physical impregnation are shown in Table 3.4. It is observed that pH_{pzc} values of support particles decreased after modification with ionic liquids, because of the electronegativity of the ionic liquids loaded.

Table 3.4 pH_{pzc} values of prepared SILP materials by physical impregnation

Support	TT600				MOX80				XAD-16			
Ionic Liquid	without	TS	A	IL	without	TS	A	IL	without	TS	A	IL
pH_{pzc}	4.317	2.083	2.667	2.053	4.064	2.10	2.064	2.073	2.412	2.143	2.00	2.061

Effect of Sorbent Dose

The amount of sorbent significantly affects the extent of Cr(VI) sorption. Increase in sorbent dose leads to more surface area for adsorption resulting in an increase in the active sites on the sorbent. The effect of adsorbent dose (g) on the adsorption of Cr(VI) was studied in the range of 0.01~0.35 g adsorbent by contacting with 10 mL of solution at 25 °C during 24 hours. The initial concentration of Cr(VI) ion was set as 50 mg/L, and pH of the solution was adjusted to the value of 4. The effects of adsorbent amount for nano particles (TT600 and MOX80) are shown in Figure 3.15 and 3.16.

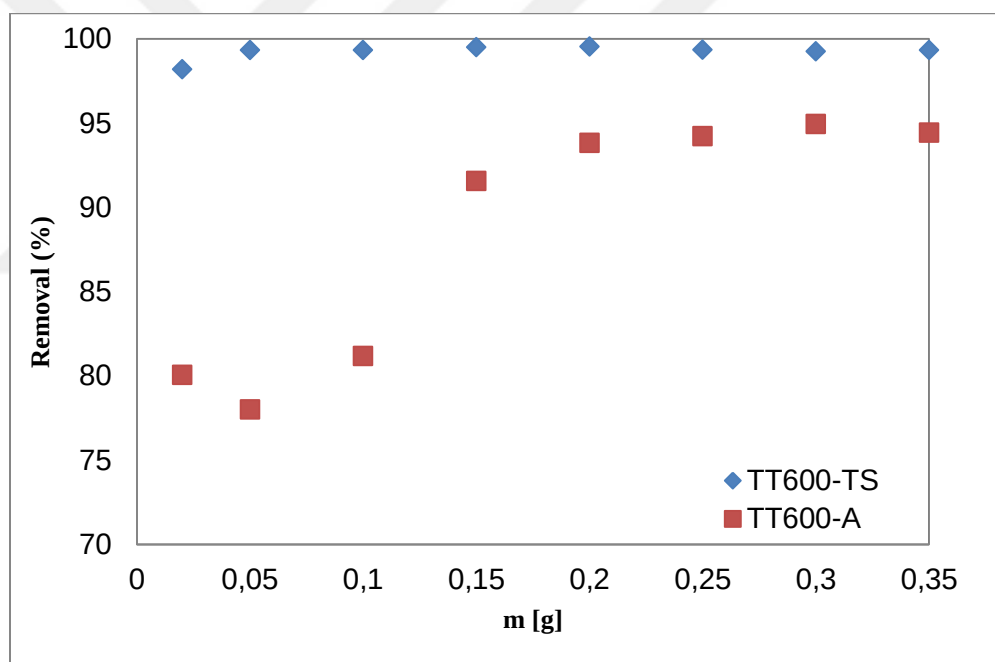


Figure 3.15 Effect of adsorbent dose on the adsorption of Cr(VI) onto SILP (TT600).

[Cr(VI)]₀= 50 mg/L, V=10 mL, m= 0.01-0.35 g, T= 25 °C, t= 24 h].

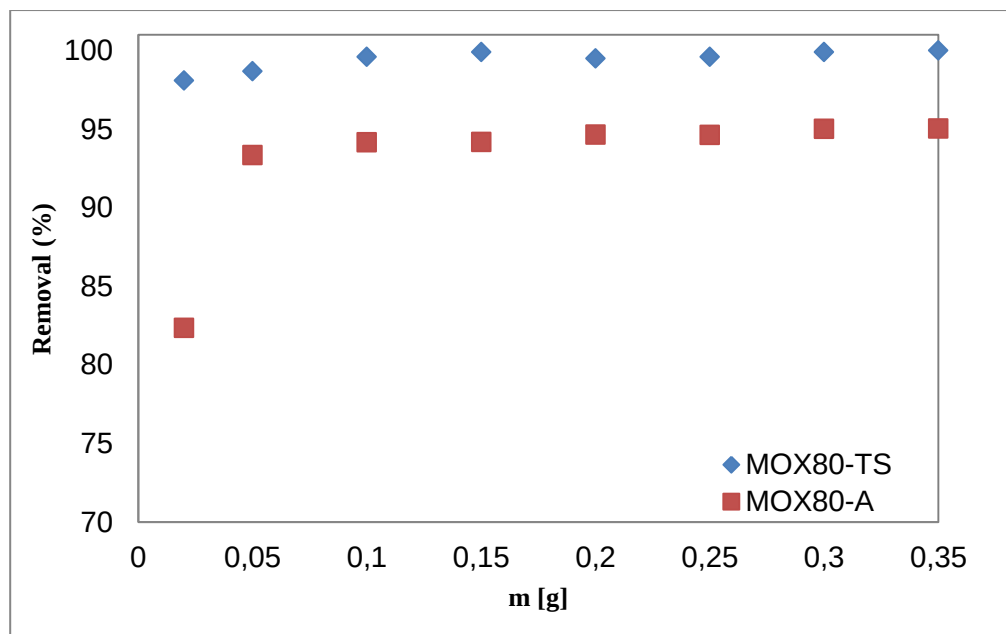


Figure 3.16 Effect of adsorbent dose on the adsorption of Cr(VI) onto SILP (MOX 80).
 $[\text{Cr(VI)}]_0 = 50 \text{ mg/L}$, $V = 10 \text{ mL}$, $m = 0.01\text{-}0.35 \text{ g}$, $T = 25 \text{ }^\circ\text{C}$, $t = 24 \text{ h}$.

It is seen from Figure 3.15 and Figure 3.16 that, TT600-TS and MOX 80-TS exhibit higher Cr(VI) sorption performance than TT600-A and MOX 80-A. The percentage removal of Cr(VI) ions increased from 82% to 94%, with the increase in the adsorbent amount of TT600-A from 0.1 to 0.2 g. Then, adsorption percentage value reached a plateau with increasing amount of the adsorbent. Therefore, for TT600-A, the optimum adsorbent dose was selected as 0.2 g for the rest of the experimental studies. In Figure 3.16, similar trend can be observed for MOX80. It can be explained that high adsorption efficiency is reached at around 0.1 g. Therefore, optimum adsorbent dose is determined as 0.1 g for MOX80-A. After this value it reaches to the plateau as seen in Figure 3.16.

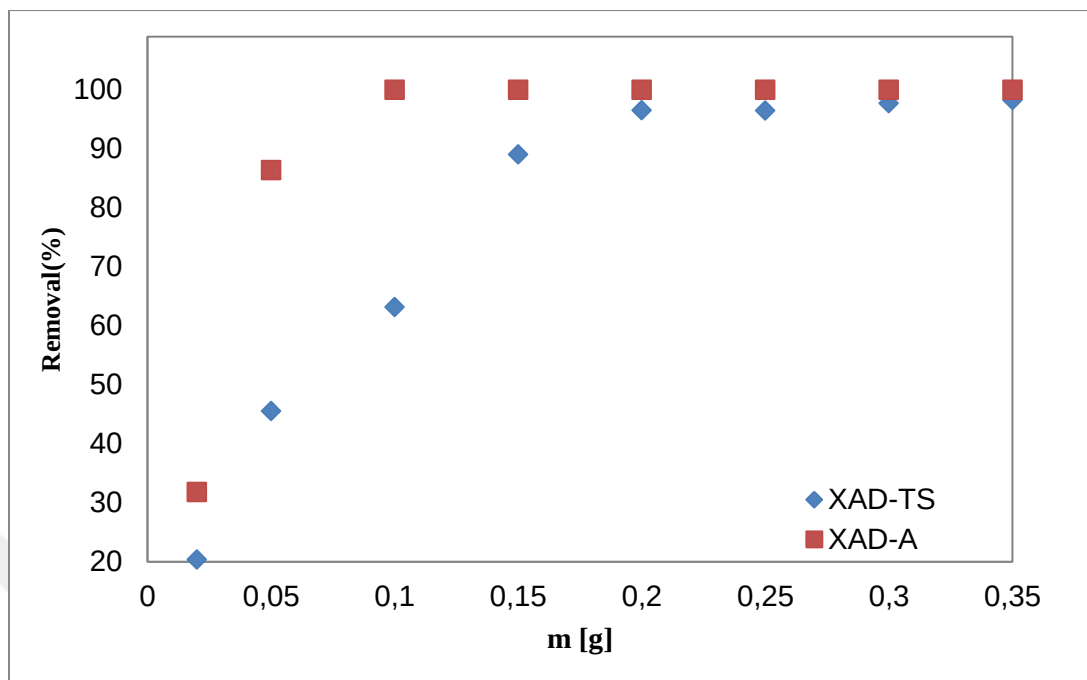


Figure 3.17 Effect of sorbent dose on the adsorption of Cr(VI) onto SILP (XAD).

$[\text{Cr(VI)}]_0 = 50 \text{ mg/L}$, $V = 10 \text{ mL}$, $m = 0.01\text{--}0.35 \text{ g}$, $T = 25 \text{ }^\circ\text{C}$, $t = 24 \text{ h}$

On the other hand, Figure 3.17 shows that polymeric adsorbents XAD-A exhibited higher performance than that of XAD-TS. While optimum sorbent dose is specified as 0.1 g for XAD-A support, 0.2 is chosen as optimum adsorbent dose for XAD-TS.

Equilibrium Studies

The equilibrium adsorption isotherms are some of the most important data for determining the sorption performances of the modified particles through the potential affinity between the metal ion and the adsorbent, the bond energy, and the sorption capacity. The adsorption equilibrium data are represented by adsorption isotherms, which correspond to the relationship between the solute concentration for the solution at equilibrium, c_e (mg/L) and the mass of the solute adsorbed per unit mass of adsorbent, q_e (mg/g) (Mahmoud, 2011).

The most commonly employed models, which are the Langmuir, Freundlich and Temkin adsorption models, were used in this study in order to describe the relationship between the amount of Cr(VI) ion adsorbed per unit weight of the modified nanoparticles (q_e) and the liquid-phase equilibrium concentration (c_e) of the Cr(VI) ions. The linear forms of the Langmuir, Freundlich and Temkin isotherms are represented by the following equations (3),(4) and (5), respectively.

Langmuir adsorption model is based on monolayer adsorption onto a surface containing energetically equivalent and fixed number of adsorption sites (Mahmoud, 2011).

$$\frac{c_e}{q_e} = \frac{1}{q_{max}b} + \frac{c_e}{q_{max}} \quad (\text{Eq. 3})$$

where c_e is the equilibrium concentration (mg/L), q_{max} is the monolayer adsorption capacity (mg/g) and b is the constant related to the free adsorption energy (Langmuir constant, L/mg).

Freundlich sorption isotherm gives an expression involving the surface heterogeneity and the exponential distribution of active sites and their energies. Also, multilayer adsorption can be possible (Fathy et al., 2015).

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \quad (\text{Eq. 4})$$

where k_f is a constant indicative of the adsorption capacity of the adsorbent (mg/g) and the constant n indicates the intensity of the adsorption.

The Temkin model describes the effect of adsorbent–adsorbate interactions which depends on binding energy. It is commonly used in the form of following equation (Javadian et al., 2013).

$$q_e = \frac{RT}{b} \ln k_t + \frac{RT}{b} \ln C_e \quad (\text{Eq. 5})$$

where $\frac{RT}{b}$, which is related to the heat of sorption, T is the temperature (K), R is the universal gas constant (8.314 J / mol K), b is the variation of sorption energy (J / mol) and k_t is the equilibrium binding constant (L / mg) corresponding to the maximum binding energy.

Equilibrium behaviours of SILPs were studied according to initial Cr(VI) concentration within the range of 20-200 mg/L by contacting with 0.2 g of SILP materials at 25°C during 24 h. Equilibrium capacities of the adsorbents (q_e) were calculated from Cr(VI) ion concentration differences of solution between initial and equilibrium conditions. Equilibrium behaviors of TT600- TS, MOX80-TS and XAD-A are shown in Figure 3.18.

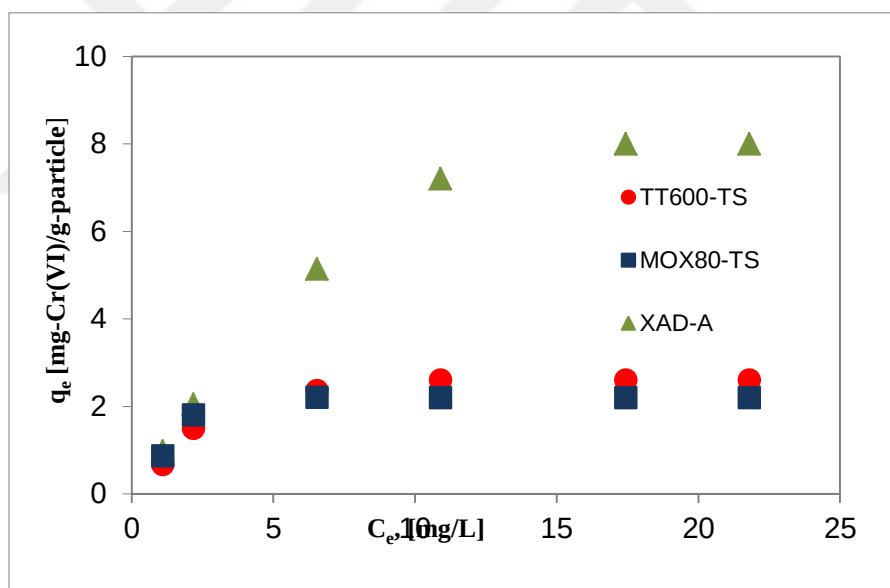


Figure 3.18 Equilibrium behavior of SILPs.

Figure 3.19, Figure 3.20 and Figure 3.21 show those adsorption fittings for the Cr(VI) ions adsorption onto SILP adsorbents.

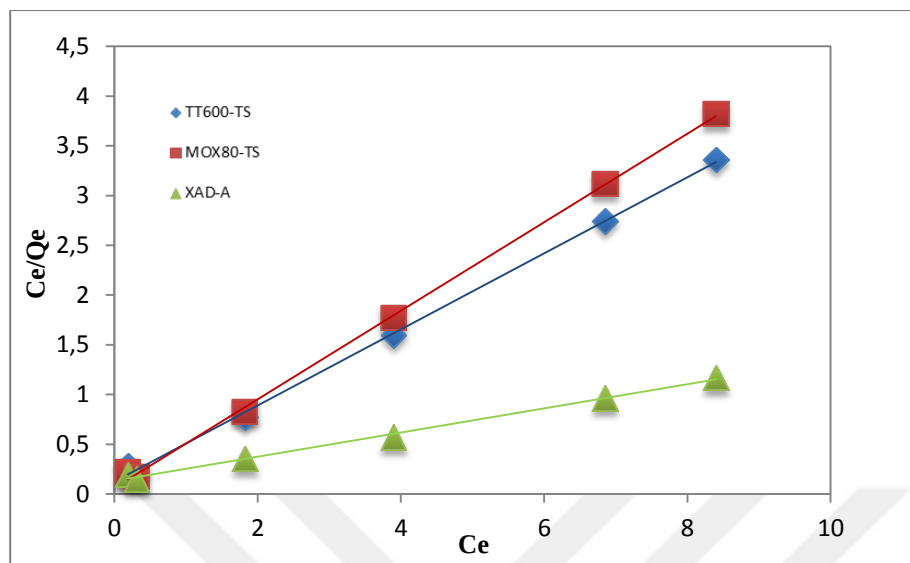


Figure 3.19 Langmuir adsorption fittings of Cr (VI) onto SILP adsorbents.

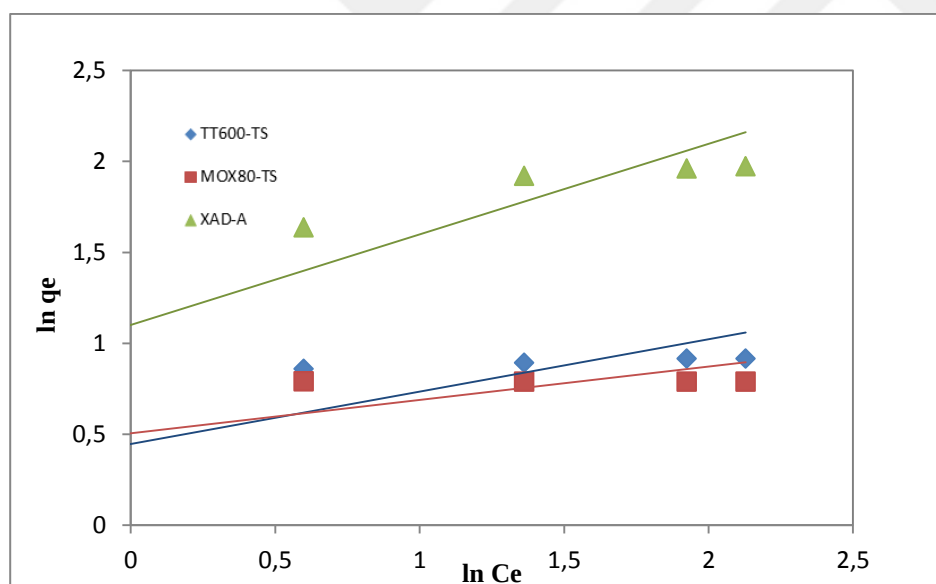


Figure 3.20 Freundlich adsorption fittings of Cr(VI) onto SILP adsorbents.

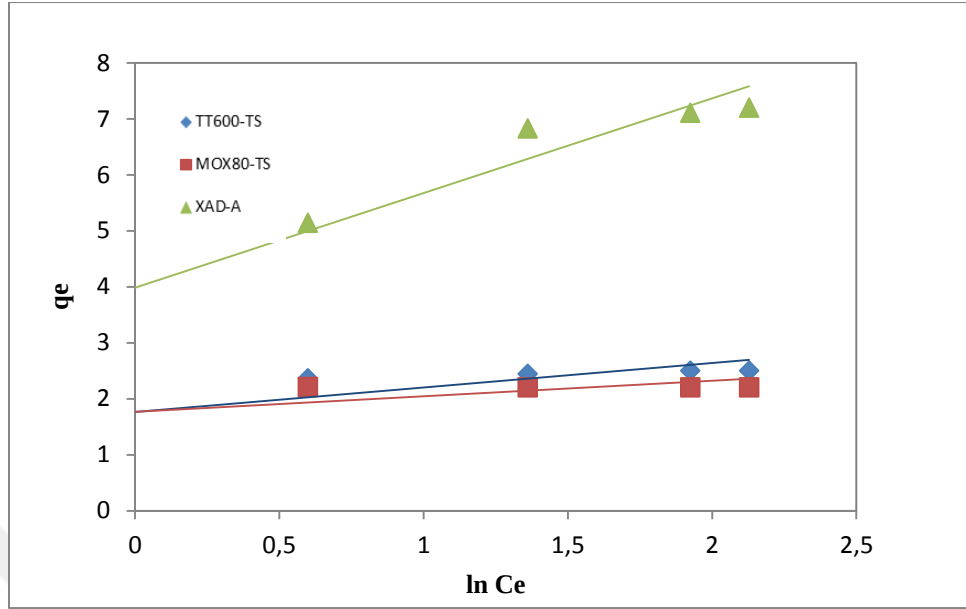


Figure 3.21 Temkin adsorption fittings of Cr (VI) onto SILP adsorbents.

Quantifying the fitness between model predictions and experimental observations, correlation coefficient (r^2) and additional three statistical measures were applied.

- The Relative Percentage Error (RPE) is used to measure the isotherm constants and compare the isotherm models. It is calculated as following equation:

$$RPE (\%) = \frac{\sum \left[\frac{|q_{calculated} - q_{experimental}|}{q_{experimental}} \right]}{N} * 100 \quad (\text{Eq. 6})$$

where N is the number of experimental data

- Mean square of residual (MSR) is calculated as following

$$MSR = \frac{\sum [q_{calculated} - q_{experimental}]^2}{N} \quad (\text{Eq. 7})$$

- An objective function (E) relating the experimental and metal uptake is defined as,

$$E = \sum \left[\frac{q_{experimental} - q_{calculated}}{q_{calculated}} \right]^2 \quad (\text{Eq. 8})$$

The Langmuir, Freundlich and Temkin adsorption isotherm constants along with the statistical coefficients are given in Table 3.5.



Table 3.5 Langmuir and Freundlich constants for the sorption of Cr(VI) on to SILPs.

MODEL	Constants	TT600-TS	MOX80-TS	XAD-A
Langmuir	q_{max} (mg/g)	2.6137	2.2452	8.2508
	b	3.0929	7.5109	0.9106
	r^2	0.9986	0.9992	0.9963
	RPE (%)	3.6983	5.4143	1.4406
	MSR	0.0260	0.0454	0.009
	E	0.1263	0.1417	0.058
Freundlich	k_f (mg/g)	1.5628	1.6562	3.0068
	n	0.2883	0.1835	0.4982
	r^2	0.7768	0.6303	0.9283
	RPE (%)	2.6142	2.1573	2.090
	MSR	0.1174	0.0942	0.2196
	E	0.3133	0.2604	0.2466
Temkin	k_t (L/mg)	56.2698	580.182	10.549
	b	5.6632	8.9262	1.4650
	r^2	0.8721	0.695	0.9862
	RPE (%)	5.3038	4.4313	2.4281
	MSR	0.0604	0.0727	0.0068
	E	0.1978	0.2024	0.0393

Equilibrium behaviour of prepared adsorbents fitted well with Langmuir Sorption Isotherm. The maximum adsorption capacities (q_{max}) for TT600-TS, MOX80-TS and XAD-A are found to be 2.61, 2.25 and 8.25 mg/g, respectively.

The agreement between Langmuir equilibrium model with the experimental equilibrium data of TT600-TS, MOX80-TS and XAD-A are shown in Figure 3.22, Figure 3.23, Figure 3.24, respectively.

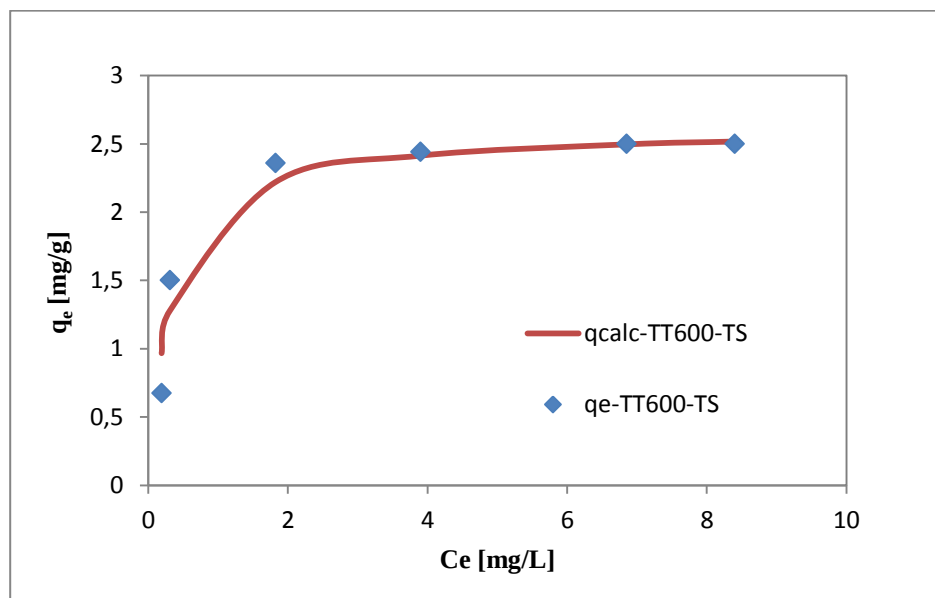


Figure 3.22 Langmuir model fits TT600-TS.

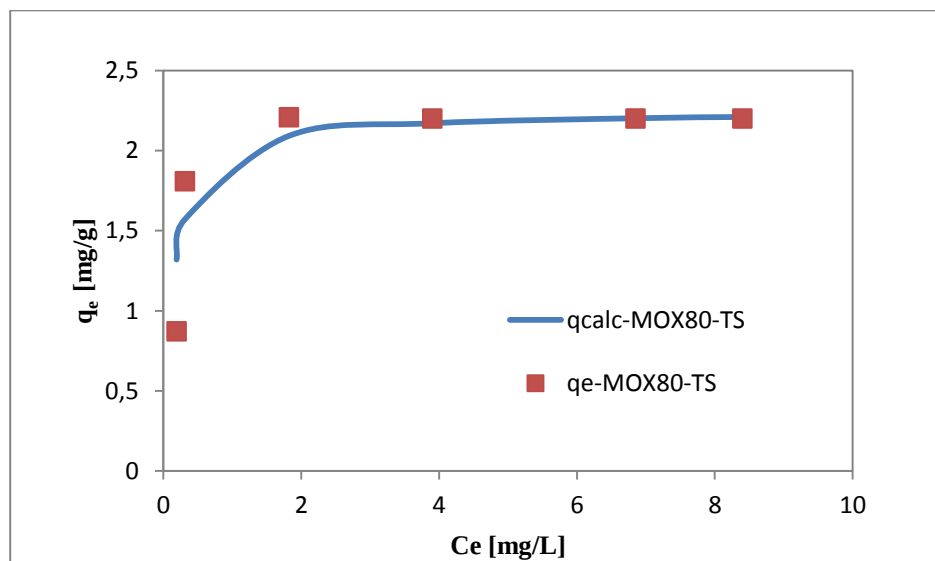


Figure 3.23 Langmuir model fits MOX80.

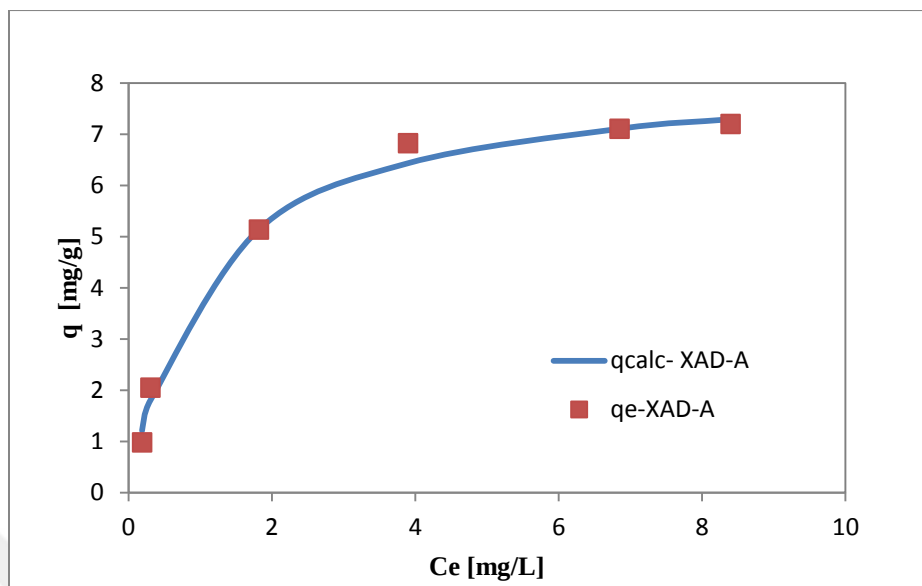


Figure 3.24 Langmuir model fit XAD-A

According to the values of correlation coefficient (R^2) for Langmuir, Freundlich and Temkin models, it can be seen that Langmuir model represents a good fit with the experimental data for all adsorbents.

3.1.3.2. Column Sorption Study

Based on the batch sorption studies, column sorption and elution studies have been carried out to investigate the breakthrough characteristics of the prepared adsorbents.

A plot of effluent metal concentration to inlet metal concentration (C/C_0) versus effluent volumes (BV) or time (t) is known as breakthrough curve. The shape and volume of breakthrough curve are crucial parameters for determining the operation and the dynamic conditions of an adsorption column (Borna et al., 2016).

The column capacity at the breakthrough point can be determined from the following equation:

$$Q_b = \frac{C_0}{m} \int_0^{Vb} \frac{(C_0 - C)}{C_0} dV \quad (\text{Eq. 9})$$

where Q_b is the column capacity at breakthrough point (mg/g), C_0 and C are the initial and effluent solution concentration (mg/L), respectively. m is the adsorbent mass (g), and Vb is the solution volume at breakthrough point. The shape and the number of bed volumes (BV) treated before the breakthrough point are very important parameters for evaluation of adsorbent performance (Borna et al., 2016).

The number of bed volumes (BV) is defined as the ratio of the volume of solution treated at breakthrough point (mL) to the volume of adsorbent bed (mL).

$$BV = \frac{\text{volume of water treated at breakthrough point [mL]}}{\text{volume of adsorbent bed [mL]}} \quad (\text{Eq. 10})$$

Total adsorbed Cr(VI) (mg/g) is calculated from the following equation:

$$Q_t = \frac{C_0}{m} \int_0^V \frac{(C_0 - C)}{C_0} dV \quad (\text{Eq. 11})$$

where Q_t is the total adsorbed Cr(VI) (mg/g), V is the solution volume, respectively.

Degree of the column utilization (CU) is calculated using the following equation:

$$CU = \frac{\int_0^{Vb} (C_0 - C) dV}{\int_0^{Veq} (C_0 - C) dV} \quad (\text{Eq. 12})$$

where Veq is the total solution volume.

Before starting the experiment, the adsorbent packed in the column was wetted with deionised water to purge the air trapped inside of the prepared particles.

0.01 M Cr (VI) solution is send through the packed bed column having 0.7 cm inner diameter downward with the help of peristaltic pump at a velocity of 5 BV/h.

Figure 3.25 shows the breakthrough curves of Cr(VI) adsorption onto SILP adsorbents prepared by physical impregnation at constant flow rate of 15 ml/min and at fixed bed height of 6 cm. The volumes of solution processed (V_b) at breakthrough point were 52 mL, 36 mL, and 20 mL for TT600, MOX80, and XAD respectively. Also, the breakthrough capacity (Q_b) was found to be 0.303 mg/g, 0.217 mg/g, and 0.152 mg/g, respectively. It is evident from Figure 3.25 that the breakthrough curves are sharp due to fast sorption kinetics and high column utilization.

The total capacities of the adsorbents prepared by physical impregnation were determined as 0.344, 0.287, 0.220 mg Cr/mL-adsorbent. Corresponding percent utilizations of the columns are calculated as 88.22, 75.39, 68.85, respectively.

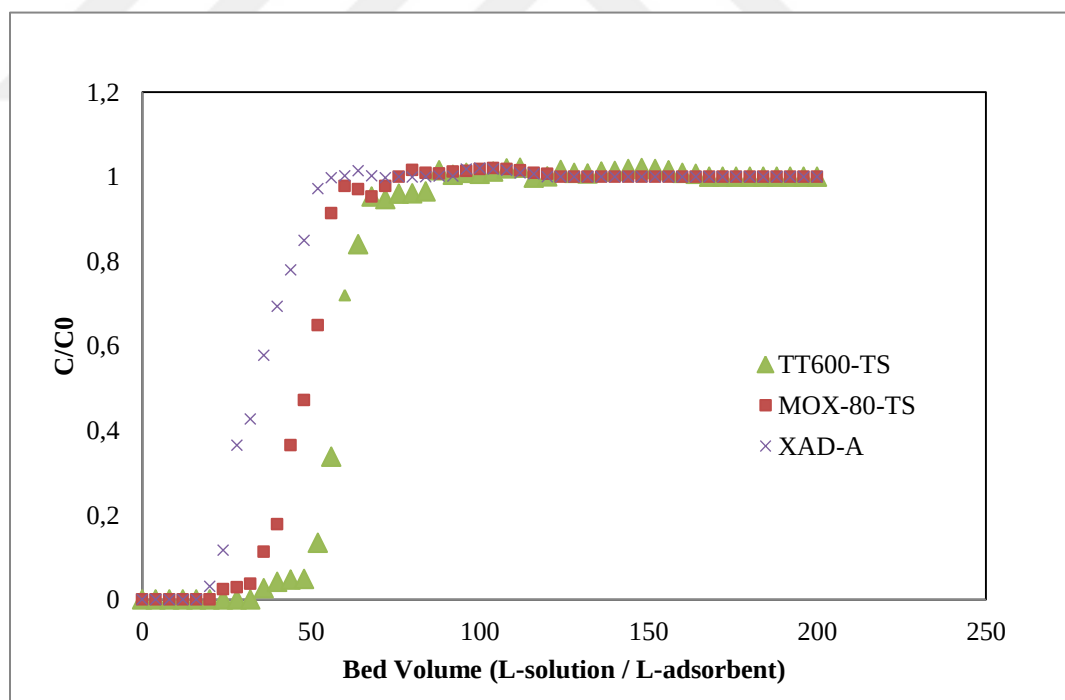


Figure 3.25 Breakthrough Curves of SILP adsorbents.

According to the literature, 0.05 mg/L is the maximum level of Cr(VI) in drinking water (WHO, 2004). Breakthrough point in column runs are determined with respect to this limit. Table 3.6 shows the operational characteristics found in column mode sorption.

Table 3.6 The results for column study for each adsorbents

	TT600- TS	MOX80-TS	XAD- A
Breakthrough point (BV)	52	36	20
Breakthrough capacity (mg Cr/mL-adsorbent)	0.303	0.217	0.152
Bed Volume BV (total)	200	200	200
Total capacity (mg Cr/mL-adsorbent)	0.344	0.287	0.220
Column utilization (%)	88.23	75.39	68.85

As it is observed, the total capacities of adsorbents TT600, MOX80, and XAD-A are found as 0.344, 0.287 and 0.220 mg Cr/mL adsorbent, respectively. As it is seen from the Table 3.6 TT600-TS has the highest column utilization with a percentage of 88.23%.

SECTION B

3.2 Supported Ionic Liquid Phase Materials Prepared by Sol-Gel Method

This section contains the results of studies conducted with sol-gel derived silica based adsorbents, which are abbreviated as SG-A, SG-TS and SG-IL according to the type of ionic liquid (A: Aliquat® 336, TS: A336][NO₃], IL: EMIMTf₂N).

3.2.1 Characterization of Adsorbents

The physicochemical characterization and surface morphology of the prepared SILP materials by sol gel method were investigated using Fourier Transform Infrared Spectrophotometer (FTIR) and Scanning Electron Microscope (SEM), respectively.

Meanwhile, the contribution of the ionic liquid on the formation of porous structure was examined by using Brunauer-Emmett-Teller (BET) analysis and thermal behavior of the materials were obtained by thermogravimetric analysis (TGA).

Physicochemical Characterization (FTIR analysis)

Changes in the chemical characteristics of sol-gel derived adsorbents with the incorporation of ionic liquid were investigated by the help of FTIR spectra presented in Figure 3.26.

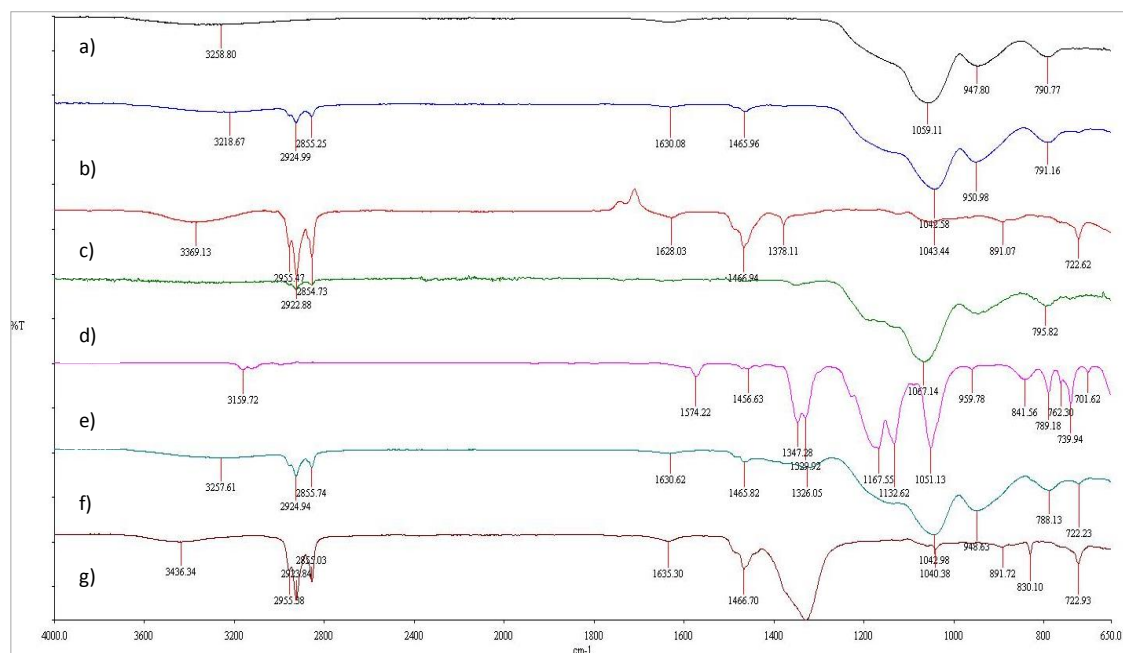


Figure 3.26 FTIR spectra of adsorbents and ionic liquids used for functionalization a) before functionalization (SG-0) b) adsorbent (SG-A) functionalized with [A336][Cl] c) ionic liquid [A336][Cl] (Aliquat 336- A) d) adsorbent (SG-IL) functionalized with EMIMTf₂N e) ionic liquid EMIMTf₂N f) adsorbent (SG-TS) functionalized with [A336][NO₃] g) ionic liquid [A336][NO₃].

In the FTIR analysis of silica material without any ionic liquid (Figure 3.26 a), the wavenumber peak at 3258.80 cm⁻¹ can be attributed as an indication of unreacted -OH structure. At this wavelength, -OH peaks are decreased or disappeared by an inclusion of the ionic liquid in the sol-gel process.

The peak located at 1465 cm⁻¹ (Figure 3.26 b) is pronounced functionalization of silica particles with [A336][Cl] ionic liquid. The FTIR spectrum of [A336][Cl] (Figure 3.10.c), the peaks around the wavenumber 2923 cm⁻¹ can be attributed to the characteristic absorption of -CH₃ of alkyl chain. The wavenumbers of 1466 cm⁻¹ and 1378 cm⁻¹ are based on the structure of quaternary ammonium moiety of the ionic liquid.

Peaks appeared at wavenumbers 3159 cm⁻¹ and 1574 cm⁻¹ (Figure 3.26 e) can be attributed as the C-H bonds of the imidazolium ring. Also, the bands around 1067 and 795 cm⁻¹ indicate the asymmetric and symmetric stretching of Si—O—Si

vibration, respectively. These data are important indications for the ionic liquids presence in SG-IL structure.

The peaks around the position of 2924 cm^{-1} can be attributed to the characteristic absorption of $-\text{CH}_3$ of alkyl chain and the bands between 1467 and 1328 cm^{-1} are based on the structure of quaternary ammonium moiety of the ionic liquid. The peak located at 1326 cm^{-1} (Figure 3.26 f) is pronounced as the functionalization of silica particles with $[\text{A336}][\text{NO}_3]$ ionic liquid.

Surface Area and Pore Properties (BET Analysis)

Surface area [m^2/g] values interms of BET, Langmuir, t-plot micropore and t-pilot external and pore width [$\text{\AA}$] values of silica based and ionic liquid functionalized silica adsorbents are shown in Table 3.7.

Table 3.7 BET analysis data of prepared adsorbents

Materials	Surface Area [m^2/g]				Pore	Pore
	BET	Langmuir	t-Plot Micropore	t-Plot External	Volume [cm^3/g]	Size [$\text{\AA}$]
SG	577.08	744.66	148.71	428.38	0.31	21.35
SG-IL	299.79	402.82	-	372.48	0.23	30.70
SG-TS	593.26	755.68	-	-	0.34	20.69
SG-A	602.35	762.34	-	-	0.32	20.33

As shown in Table 3.7 sol-gel derived adsorbents functionalized with various type of ionic liquids were characterized to be mesoporous with average pore diameter of 2 nm and BET surface area in the range of $300\text{--}600\text{ m}^2/\text{g}$. Pore volumes of SG-TS and SG-A are higher than those of SG (untreated) type adsorbents while average pore diameters of adsorbents containing TS and A type ionic liquid are lower than those of SG leading to higher surface area. On the other hand, BET surface area of sol-gel

derived adsorbents decrease with incorporation of IL type ionic liquid. This situation may be attributed that the surface are occupied by the long alkyl chain of EMIMTf₂N.

Morphological Characterization (SEM Analysis)

The morphological characteristics of SG-A, SG-TS and SG-IL were evaluated by using a Scanning Electron Microscope (SEM) as shown in Figure 3.27.

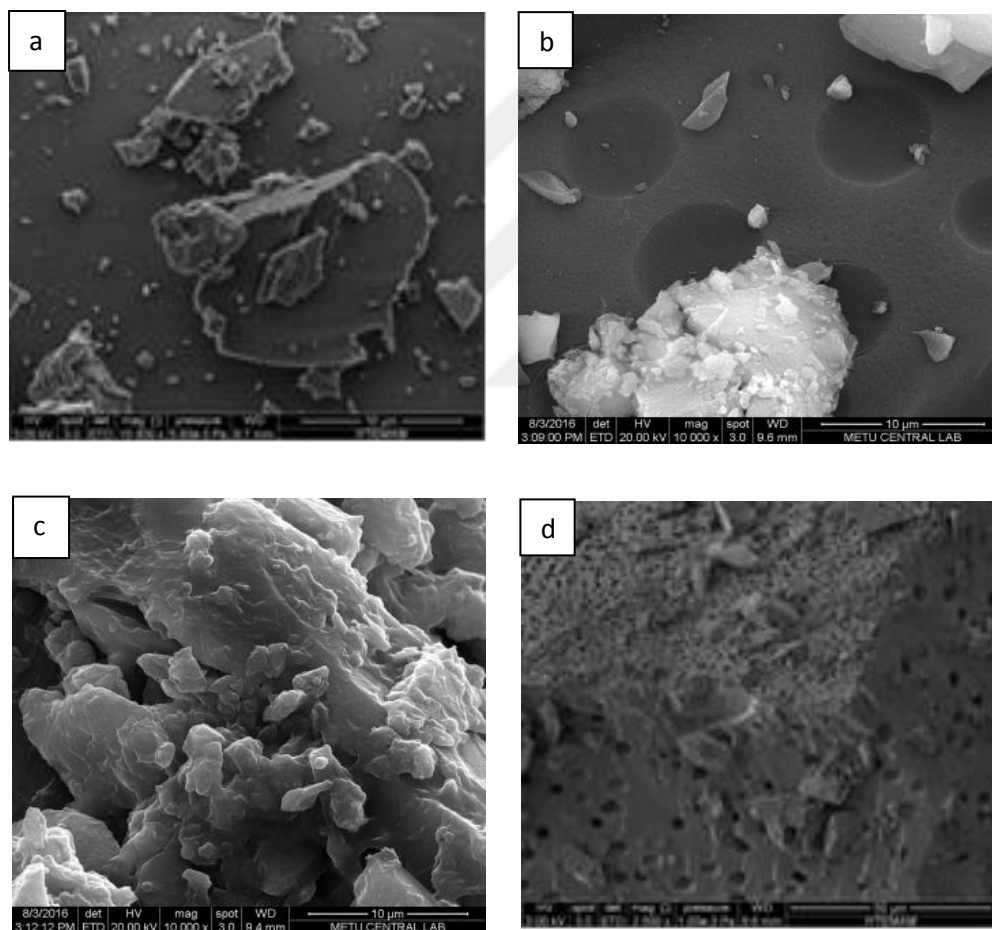


Figure 3.27 SEM images of prepared adsorbents with the magnification rate of 10000 a) SG-0, b) SG-A, c) SG-TS, d) SG-IL.

In the SEM images of silica materials having no IL content, it is observed that, the surface area of SG-0 have nonporous and nonhomogeneous structures.

Unreacted residues are evident on the surface of the material. Pore structure formation are observed by presence of the ionic liquid especially, Aliquat 336, (SG-A) and imidazolium based IL, EMIMTf₂N, (SG-IL). On the other hand, [A336][NO₃] (SG-TS) is seemed that task specific IL covers the surface of the silica particles which can led to a decrease in the surface area by modification.

Thermal Stabilities of Prepared Adsorbents (TGA Analysis)

The effect of ionic liquid on the thermal behavior of the silica particles was investigated using by Thermal Gravimetric Analysis (TGA) at the temperature range of 0-600 °C. The thermogravimetric profiles of prepared adsorbents are given in Figure 3.28.

In all thermal behavior characteristics of the prepared adsorbents by sol-gel, they are started to decompose at higher temperatures, because of the high thermal stability of ionic liquids. As shown in the graph of A336 [NO₃] and A336 [Cl] ionic liquids, they start to decompose moderately at high temperature around 250 °C. A large proportion of weight loss occurs above 250 °C, indicating that sol-gel particles in the presence of ionic liquids have good thermal stability.

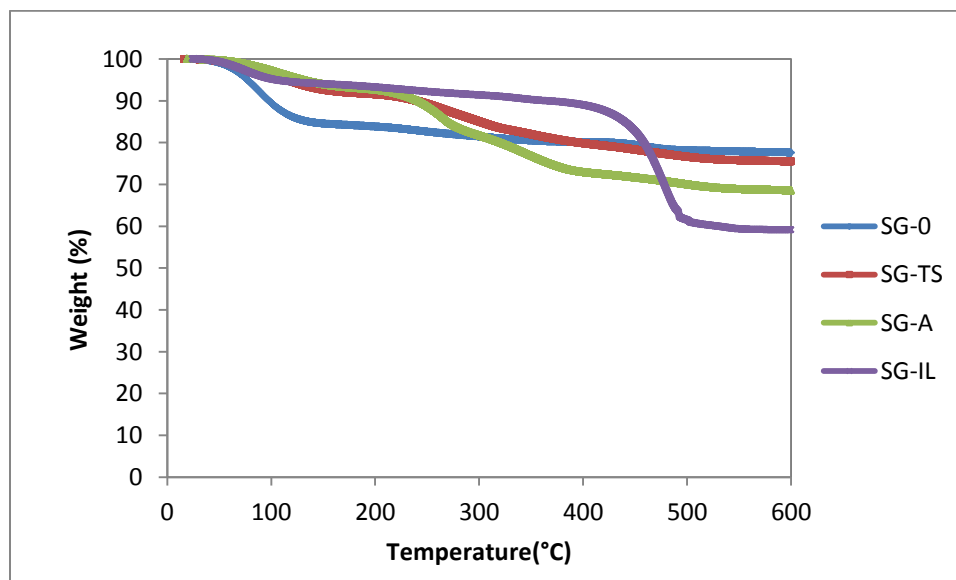


Figure 3.28 TGA thermograms of SG-IL adsorbents.

In TGA profiles (Figure 3.29), silica adsorbents without IL content (SG-0) is started to decompose at low temperatures around 50 °C. The adsorbents containing imidazolium based ionic liquid with the weight percentages of 20 and 40, have a weight loss at the higher temperatures because of high thermal stability of IL. It can be concluded that IL increases thermal stability of silica materials.

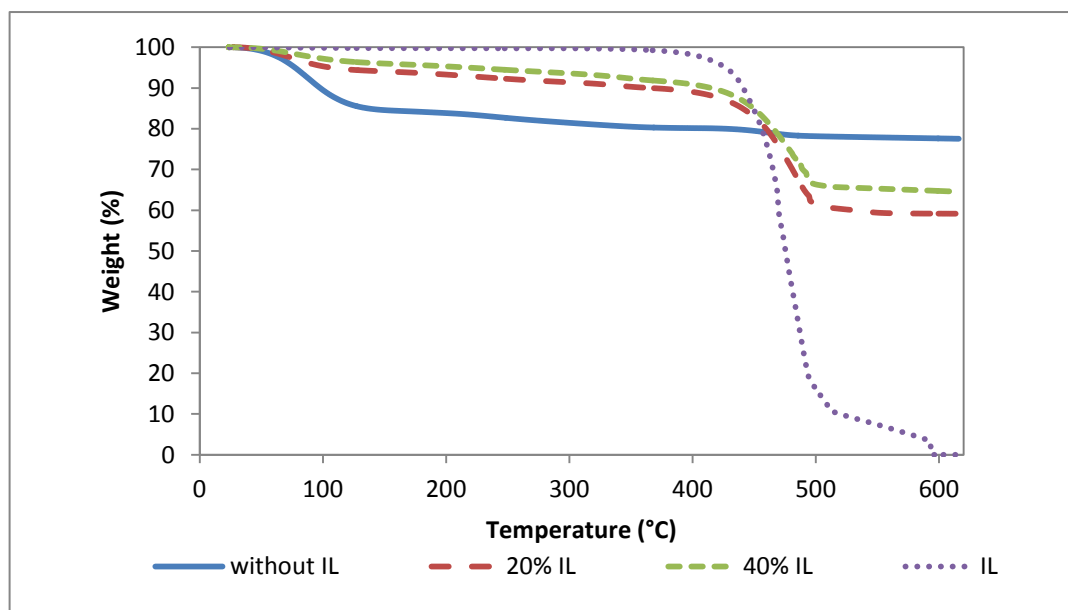


Figure 3.29 TGA thermograms of SG-IL adsorbents.

3.2.2 Sorption Performance of Prepared Adsorbent by Sol Gel

Sorption performances of the adsorbents prepared by sol gel were investigated by considering sorption of Cr(VI) ions from aqueous solution.

3.2.2.1 Batch Sorption Studies

The sorption performances of sol-gel derived adsorbents containing various type of ionic liquid were evaluated as removal percentage of Cr(VI). The effect of adsorbent amount (0.01-0.3 g), initial Cr(VI) ion concentration (5–700 mg/L), pH of the solution (0-12) and the temperature of the operation were examined. In addition,

effect of ionic liquid amount included during sol-gel synthesis on the mass basis such as 0.5 and 0.7 g-IL/g-silica precursor (TEOS).

Effect of IL type on the sorption of Cr (VI) ions

Figure 3.30 illustrates the removal performance of silica based adsorbents synthesized by using various type of ionic liquids for the sorption of Cr(VI) ions.

It can be confirmed from Figure 3.30 that silica based materials prepared by sol-gel method using tricapryl methyl ammonium chloride [A336][Cl] ionic liquid showed better removal efficiency for Cr(VI) in comparison to other functionalized adsorbents. For further studies, the material synthesized by sol-gel method with using [A336][Cl] ionic liquid was chosen as a suitable sorbent. Although the removal efficiency results of SG-A and SG-TS were quite similar, SG-A type adsorbents was chosen. Because of the fact that SG-TS needs an additional step during synthesis comparing with the preparation route of SG-A.

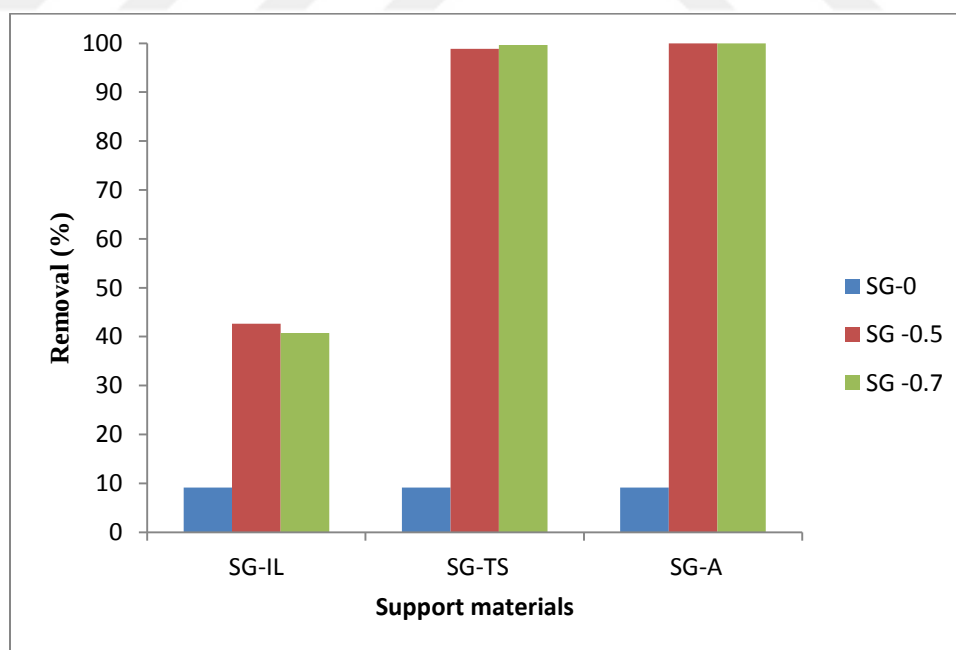


Figure 3.30 Removal efficiency of silica based adsorbents containing various type of ionic liquids.

[Cr(VI)]₀ = 50 mg/L, V = 10 mL, m = 0.2 g, T = 25 °C, t = 24 h].

Sorption percentage of the adsorbents have been enhanced by containing Aliquat 336 type ionic liquid (SG-A) up to 99%. Adsorption capacity of SG-A type adsorbents was computed as 34.74 mg/g and it is also observed that the increase in IL content has no pronounced effect on the sorption performances.

Effect of Adsorbent Amount

The effect of adsorbent amount (g) on the adsorption of Cr(VI) was studied in the range of 0.01~0.3 g adsorbent by contacting with 10 mL of solution at 25 °C during 24 hours. The initial concentration of Cr(VI) ion was set as 50 mg/L. The effects of sorbent dosage of prepared materials with sol-gel method on Cr(VI) removal from aqueous solution are shown in Figure 3.31

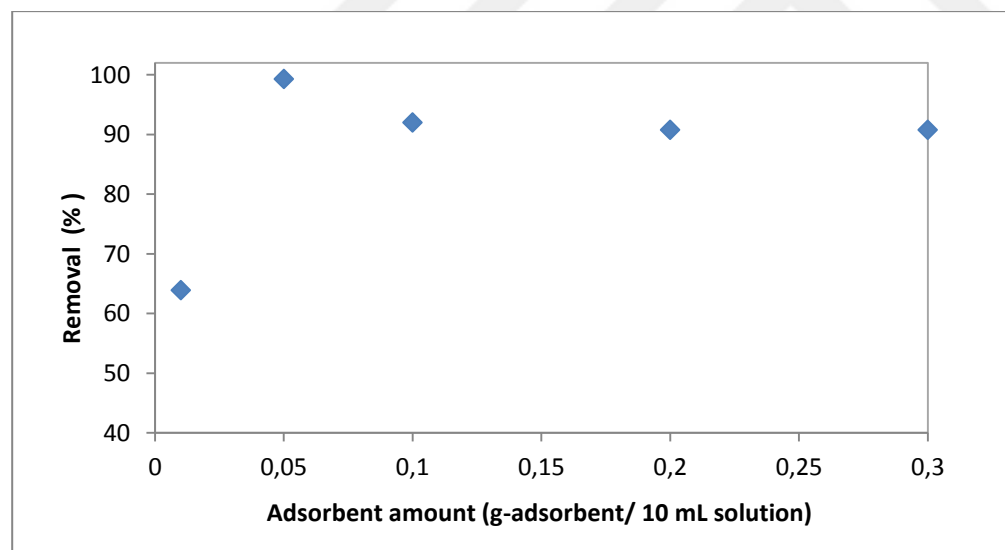


Figure 3.31 Effect of sorbent dose on the adsorption of Cr (VI) onto mesoporous silica(SG-A).

[Cr(VI)]₀= 50 mg/L, V= 10 mL, m= 0.01-0.3 g, T= 25 °C, t= 24 h].

It can be noticed that an increase in adsorbent amount from 0.01 to 0.05 g leads to an increase in the uptake amount of Cr(VI) onto the adsorbent, then there is no significance effect from 0.1 to 0.3 adsorbent/10 mL-solution. Because of the fact that after a certain amount of adsorbent, the maximum adsorption was obtained and

the amount of ions connected to the adsorbent and the amount of free ions remains constant even with further addition of the amount of adsorbent.

Effect of solution pH

Solution pH is one of the important adsorption parameters that affect the adsorption behavior of metal ions in aqueous solution. Metal adsorption behaviour of the solution is extremely related to the surface functional groups in the sorbent and metal solution chemistry (Dehghani, et al., 2016)

The sorption performances of prepared adsorbents at the pH range of 2-7 are shown in Figure 3.32.

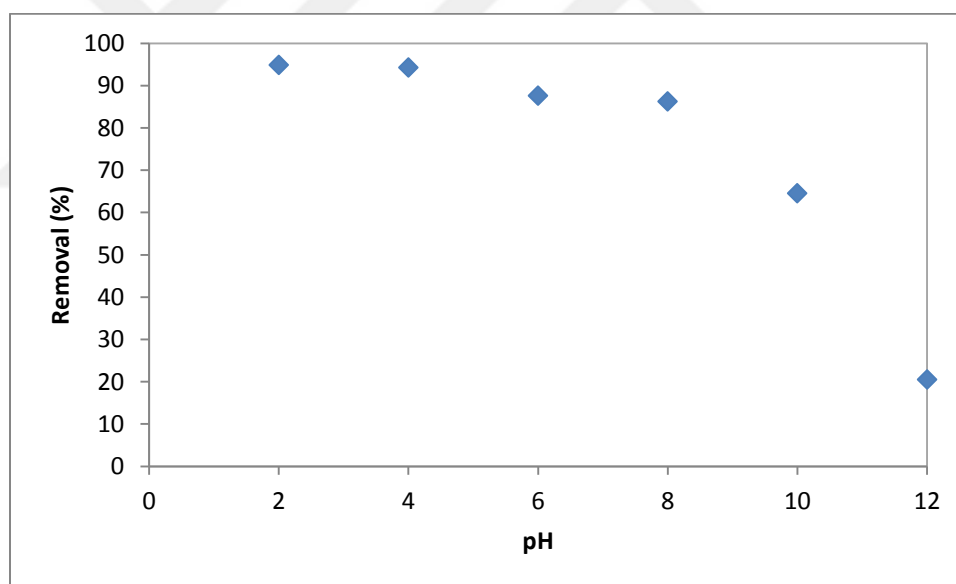


Figure 3.32 Effect of pH on the adsorption of Cr (VI) onto adsorbent.

[Cr(VI)]₀ = 50 mg/L, V = 10 mL, m = 0.05 g, T = 25 °C, t = 24 h].

At a lower pH range of 2–4, the dominant form of Cr (VI) is $(\text{HCrO}_4)^-$ and above pH 6.0 Cr(VI) exists as $(\text{CrO}_4)^{2-}$. The adsorbent surface is positively charged at lower pH, that lead to strong electrostatic attraction between positively charged adsorbent surface and negatively charged chromium ions.

The overall surface charge on the adsorbents became negative with increasing pH value, thereby adsorption performance decreases. Hence, at pH values ranging from 2 to 4 adsorbent shows better removal efficiency for Cr(VI) ions. For this reason pH 4 can be taken as the optimum pH value.

Effect of Temperature on the Sorption of Cr(VI) ions

The effect of temperature on the adsorption of Cr(VI) on the SG-A adsorbent was investigated within the range of 15-40 °C with initial concentration of 50 mg/L.

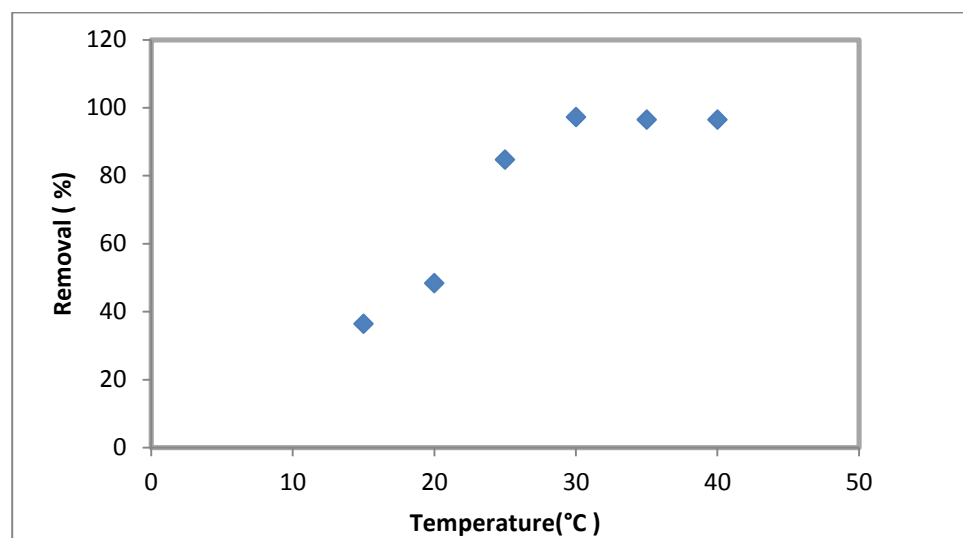


Figure 3.33 Effect of temperature on the adsorption of Cr (VI) onto SG-A

[Cr(VI)]₀= 50 mg/L, V= 10 mL, m= 0.05 g, T= 25 °C, t=24 h].

The results shown in Figure 3.33 point out that the percentage removal of Cr(VI) increased from 40% to 98% with the increasing in the temperature from 15 to 40°C which indicated the endothermic nature of the process. A maximum removal value of 97.25% of chromium ions was obtained at the temperature value of 30 °C.

The increase in sorption with temperature may be based on increasing in the number of active surface sites available for sorption on the adsorbent or the mass transfer resistance of adsorbate in the boundary layer decreased since that in connection with the decreasing in the boundary layer thickness surrounding the sorbent. Also increasing adsorption with rising the temperature may be by reason of

the reinforcement of adsorptive forces between the active sites of the sorbents and adsorbate species and between the adjacent molecules of the adsorbed phase (Javadian et al., 2013).

Effect of Temperature on Thermodynamic Parameter on Adsorption of Cr(VI)

In order to better understand the effect of temperature on the adsorption of the Cr(VI) ions onto SG-A adsorbent, three basic thermodynamic parameters which are enthalpy change ΔH° , free energy change ΔG° and entropy change ΔS° were studied. These parameters were calculated using Equations (13-15).

$$\Delta G^\circ = -RT \ln K_d \quad (\text{Eq. 13})$$

where K_d is the metal distribution ratio between adsorbent phases and solution ($K_d = \frac{q_e}{C_e}$ (L/g)). The values of K_d can be determined by plotting $\ln(q_e/C_e)$ versus q_e and extrapolating to zero, where q_e is the adsorbed Cr(VI) ions concentration at equilibrium and C_e is the equilibrium concentration of Cr(VI) ions in solution (Arshadi et al., 2014).

The ΔH° and ΔS° values were calculated from slope and intercept of the linear plot, of $\ln K$ vs $1/T$ as shown in Figure 3.34 a.

$$\ln K_d = \frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (\text{Eq. 14})$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (\text{Eq. 15})$$

As seen in Figure 3.34-b, the values of ΔS° and ΔH° were calculated from the intercept and slope of a plot of ΔG° versus T according to Equation (15) by linear regression analysis. R is the universal gas constant (8.314 J/molK) and T is the

absolute temperature in Kelvin (K) (Jayakumar and Rajasimman, 2014). The calculated thermodynamic parameters were listed in Table 3.8.

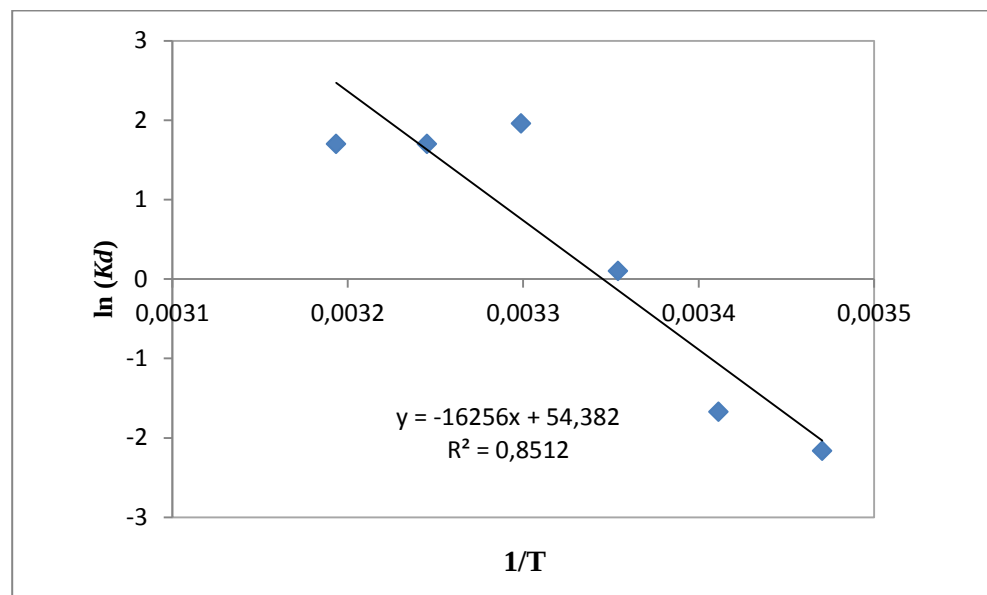


Figure 3.34 a – Arhenius plot of Cr(VI) adsorption by studied material.

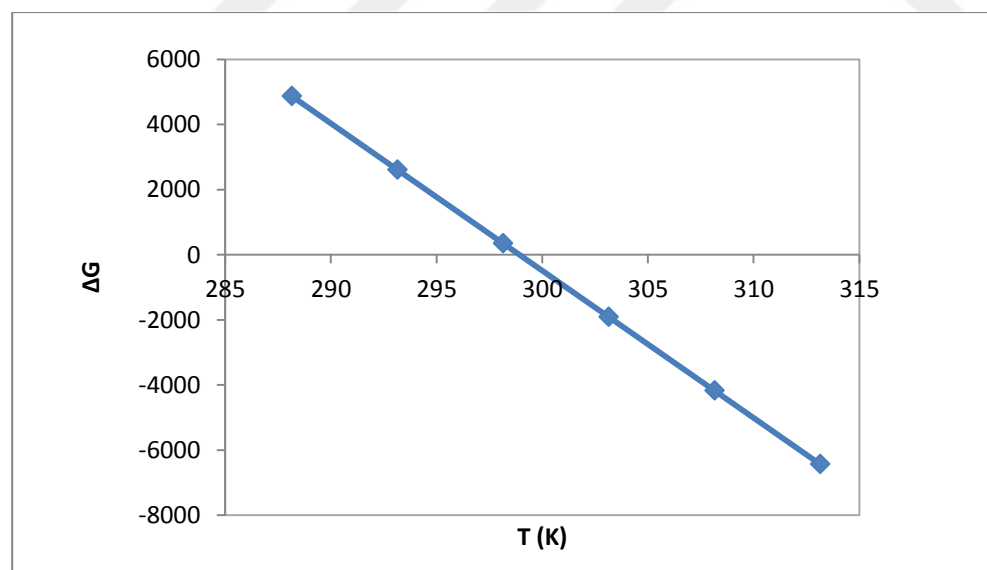


Figure 3.34 b – Plot of ΔG° versus T for the estimation of thermodynamic parameters for sorption of Cr(VI) by studied material.

Table 3.8. Thermodynamics parameter for the sorption of Cr(VI) by SG-A adsorbents

ΔH (kJ/mol)	ΔS (J/mol.K)	ΔG (kJ/mol)					
		15° C	20° C	25° C	30° C	35° C	40° C
		ΔG					
135.153	452.1319	4.870	2.610	0.349	-1.911	-4.172	-6.43
		K_d (L/g)	0.114	0.187	1.107	7.085	5.467

The positive ΔH (kJ/mol) values as shown in Table 3.8 indicated that the adsorption process was endothermic. In low temperature values, K_d value was found to be lower than 1. This situation shows that adsorption tendency of chromium ions is unfavorable. When the temperature increased above 25° C, the molecules chose to be in solid phase. This situation is also confirmed with ΔG values. ΔG values were negative under 25 °C and above 25 °C ΔG values had a reverse situation, were positive. Additionally, the positive values of ΔS was a sign that the degrees of randomness increased at the solid-liquid interface during the adsorption of Cr(VI) ions and reflected the affinity of the adsorbent.

Equilibrium Studies

The effect of Cr(VI) concentration on the sorption performance of SG-A type adsorbent is shown in Figure 3.35.

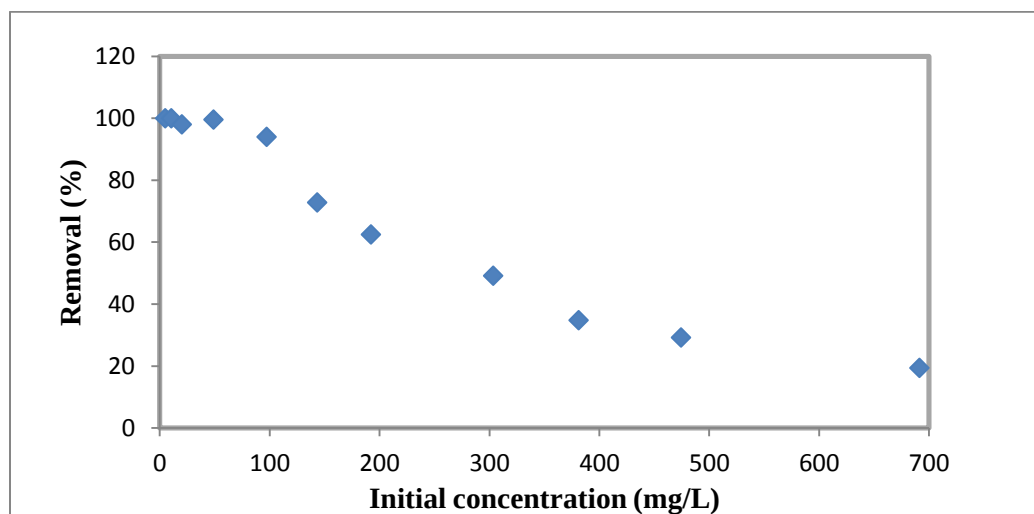


Figure 3.35 Effect of initial concentration of Cr(VI) ions on the removal performance of SG-A adsorbents
 $[\text{Cr(VI)}]_0 = 5\text{--}700 \text{ mg/L}$, $V = 10 \text{ mL}$, $m = 0.05 \text{ g}$, $T = 25^\circ \text{C}$, $t = 24 \text{ h}$

As seen in Figure 3.35, the effect of initial Cr (VI) concentration from 5 to 700 mg/L with adsorbent amount of 0.05 g at pH of 4.0 was investigated. The adsorption of Cr (VI) on adsorbent decreased from 100% to 19.40% by increasing the Cr (VI) concentrations from 5 mg/L to 700 mg/L respectively.

The decrease in chromium adsorption from 100% to 19.40% could be due to the lack of available binding sites required for the high initial concentration of chromium, whereas the higher uptake of chromium at low concentration due to more metal ions were left unadsorbed in solution at higher concentration levels.

Effect of initial concentration of Cr(VI) ions on the adsorption capacity of SG-A type adsorbent is also shown in Figure 3.36.

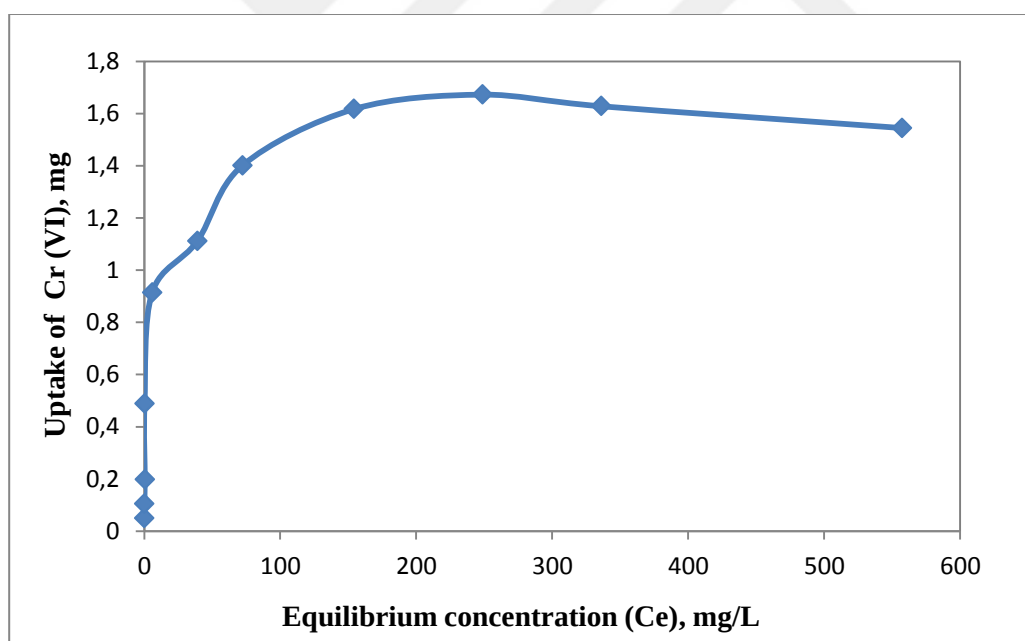


Figure 3.36 Effect of initial concentration of Cr(VI) ions on the Cr(VI) uptake of SG-A adsorbents.

$[\text{Cr(VI)}]_0 = 5\text{--}700 \text{ mg/L}$, $V = 10 \text{ mL}$, $m = 0.05 \text{ g}$, $T = 25 \text{ }^\circ\text{C}$, $t = 24 \text{ h}$.

It is evident from Figure 3.36, the sorption capacity of the SG-A type adsorbent increases with the increasing initial Cr(VI) ion concentration. Equilibrium curve reaches plateau with the adsorption capacity value of 35

mg-Cr(VI)/g-adsorbent. Then the increasing in the solution concentration has no significance effect on the uptake of Cr(VI).

In order to obtain information about the properties and the mechanism of the adsorption process several sorption equilibrium model proposed in the literature such as Langmuir, Freundlich and Temkin isotherm models.

Experimental adsorption equilibrium data of Cr (VI) heavy metal ions on SG-A adsorbent were fitted by applying these models corresponding to Equations (4-5-6) (in Section A).

Figure 3.37 shows the linearized Langmuir plots of Cr(VI) sorption isotherms for SG-A. The capacity Q_{max} (mg/g) and constant b (mg/L) calculated from model equation are tabulated in Table 3.9. Based on this table, it can be concluded that SG-A may be a good candidate as an adsorbent for the removal of Cr(VI) from aqueous solution.

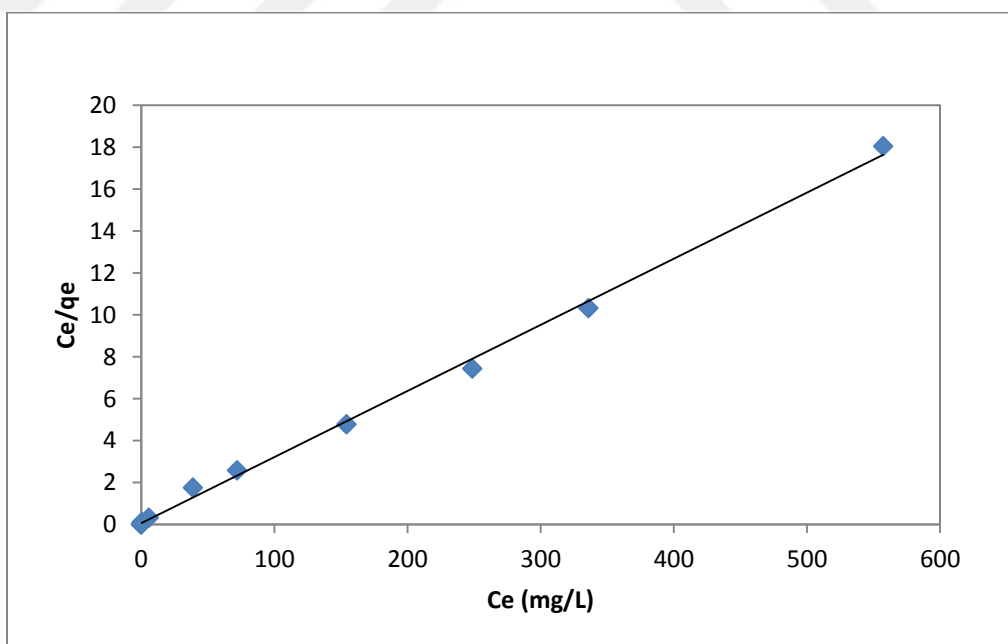


Figure 3.37 Linearized Langmuir isotherm plots for the sorption of Cr(VI) onto SG-A at 25 °C.

Figure 3.38 shows the linearized Freundlich plots of Cr(VI) sorption for SG-A at different initial metal concentration and the constants k_f and n were tabulated in

Table 3.10. The values of k_f (mg/g) and $1/n$ were calculated from the intercept and slope of the plot between $\ln(q_e)$ versus $\ln(C_e)$. Langmuir equation fits the experimental data better than the Freundlich equation.

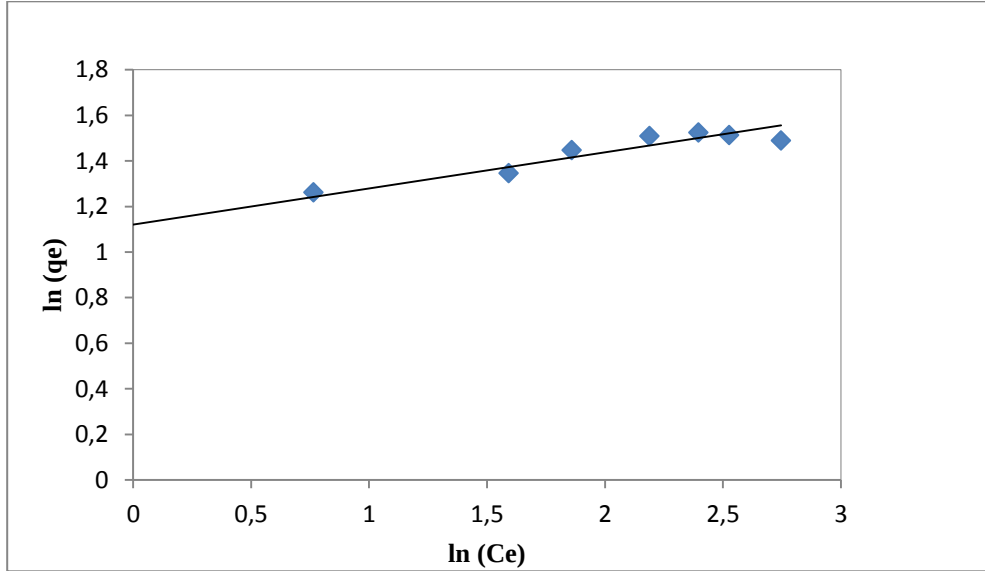


Figure 3.38 Linearized Freundlich isotherm for the sorption of Cr(VI) onto SG-A at 25 °C.

The values of k_t and b in Temkin isotherm can be calculated from the linear plot of q_e versus $\ln(C_e)$ (Figure 3.39). Data given in Table 3.9 show that the correlation coefficient of Langmuir model are higher than that of Temkin model.

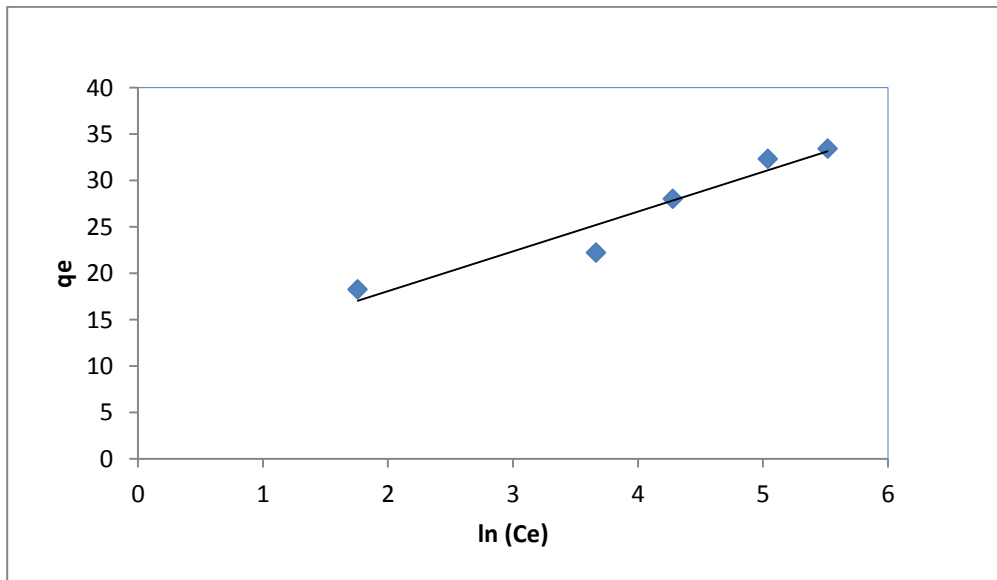


Figure 3.39 Linearized Temkin isotherm for the sorption of Cr(VI) onto SG-A at 25 °C.

Table 3.9 Values of linearized isotherm models

MODEL		CONSTANTS				
	q_{max} (mg/g)	b	R^2	RPE (%)	MSR	E
Langmuir	31.74	1.48	0.99	30.30	29.81	0.78
	k_f (mg/g)	n	R^2	RPE (%)	MSR	E
Freundlich	3.06	6.31	0.96	-71.84	386.78	89.18
	k_t (L/mg)	B	R^2	RPE (%)	MSR	E
Temkin	9.15	4.28	0.93	6.63	65.80	2.24

Consequently, among the three isotherm models applied it is clear that Langmuir isotherm with the maximum sorption capacity of 31.74 mg/g offers the best correlation factor ($R^2=0.99$). The Langmuir model suggests homogeneous surface and monolayer adsorption process which indicates active sites are well distributed throughout the SG-A.

Kinetic Modeling

Kinetic behavior of adsorbents is of significant importance in the adsorption processes. In this study, the adsorption of the Cr(VI) onto SG-A was studied as a function of contact time to determine the kinetic behavior of prepared adsorbents.

Fractional attainment of equilibrium (X) was determined by calculating the ratio of the concentration of chromium ions at any time, C , with the concentration of chromium ions at equilibrium, C_e .

$$X = \frac{C}{C_e} \quad (\text{Eq.16})$$

Figure 3.40 shows the change in X with respect to time. It is evident that the fractional attainment of equilibrium increased from 0.08 to 1 with the increasing in the time from 5 to 240 min. As seen Figure 3.40, the required contact time to reach the equilibrium of Cr(VI) is found as 4 hours (240 min).

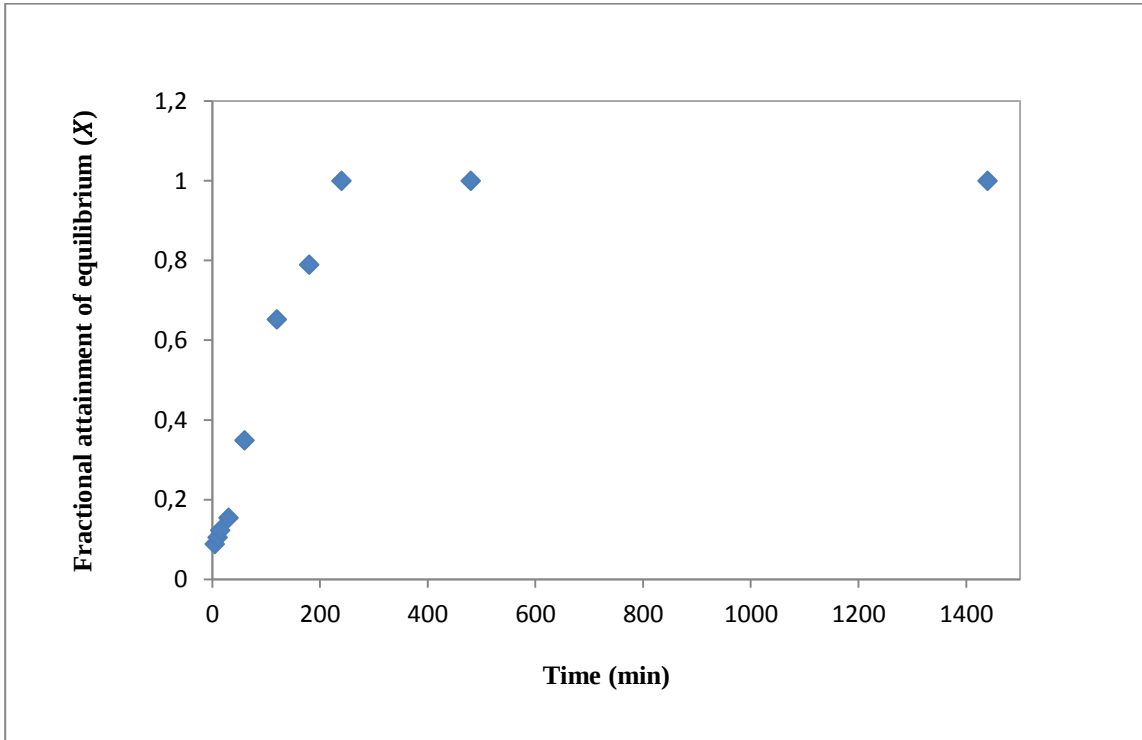


Figure 3.40 Effect of contact time on the adsorption of Cr(VI).

Several kinetic models have been applied to examine the controlling mechanism of Cr(VI) ion sorption onto SG-A. Some conventional models as pseudo first order, pseudo second order and intra particle diffusion (Weber and Morris) and Elovich model were applied to interpret the experimental results. In addition to them, some diffusional models such as the infinite solution volume (ISV) model and the unreacted core model (UCM) were used in order to describe the rate determining steps in the ion exchange process.

One of the kinetic equations most widely used for the sorption from a liquid solution is Pseudo first order equation. Lagergren equation is given as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (\text{Eq. 17})$$

where k_1 is the rate constant of pseudo-first-order sorption (min^{-1}), q_e and q_t are the amounts of Cr(VI) sorbed at time t and at equilibrium (mg/g), respectively.

After integrating the Eq.17 with, the boundary conditions ($q_t = 0$ at $t = 0$ and $q_t = q_e$ at $t = t$);

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \quad (\text{Eq. 18})$$

A plot of $\log(q_e - q_t)$ versus t should give a straight line to confirm the applicability of the kinetic model as shown in Figure 3.41.

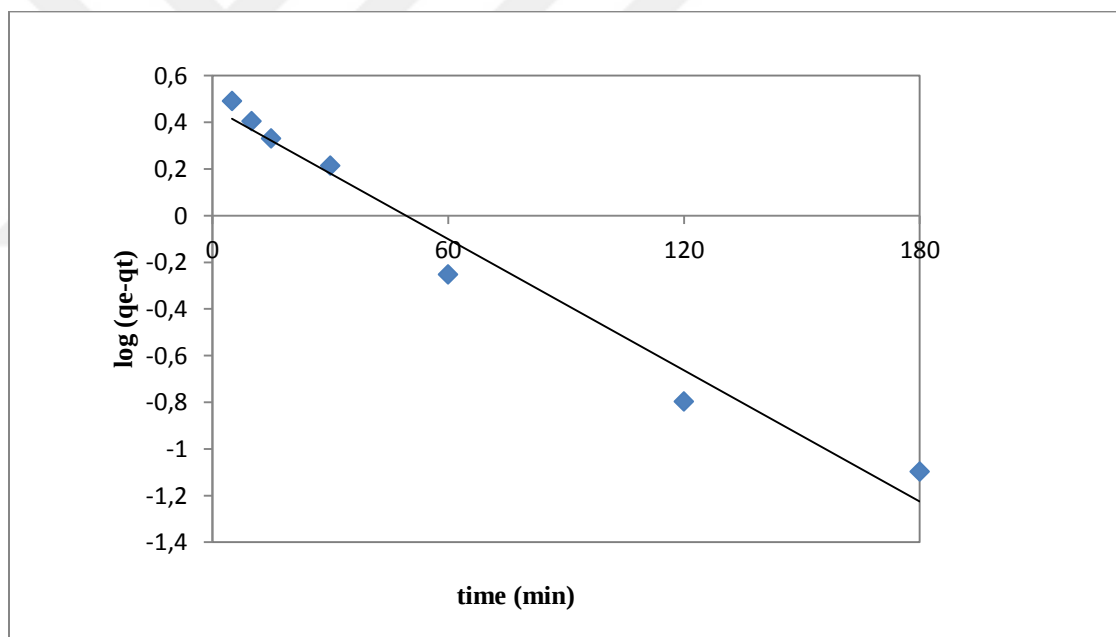


Figure3.41 Pseudo first order plots for the sorption of Cr(VI) onto SG-A.

The pseudo-second-order equation is also based on the sorption capacity of the solid phase. Contrary to the first order model, it predicts the behavior over the whole time adsorption and it is in agreement with an adsorption mechanism being the rate controlling step.

Based on the sorption equilibrium capacity, a pseudo-second order equation can be written as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t)^2 \quad (\text{Eq. 19})$$

If the rate of sorption is a second-order mechanism, the pseudo-second-order chemisorption kinetic rate linearized equation is expressed as follows (Dundar and Nuhoglu, 2008)

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (\text{Eq. 20})$$

where k_2 (g/mg min) is the pseudo-second-order rate constant of adsorption. The plot t/q versus t (Figure 3.42) should give a straight line if second order kinetics are applicable and q_e and k_2 can be determined from the slope and intercept of the plot, respectively. The results are given in Table 3.10.

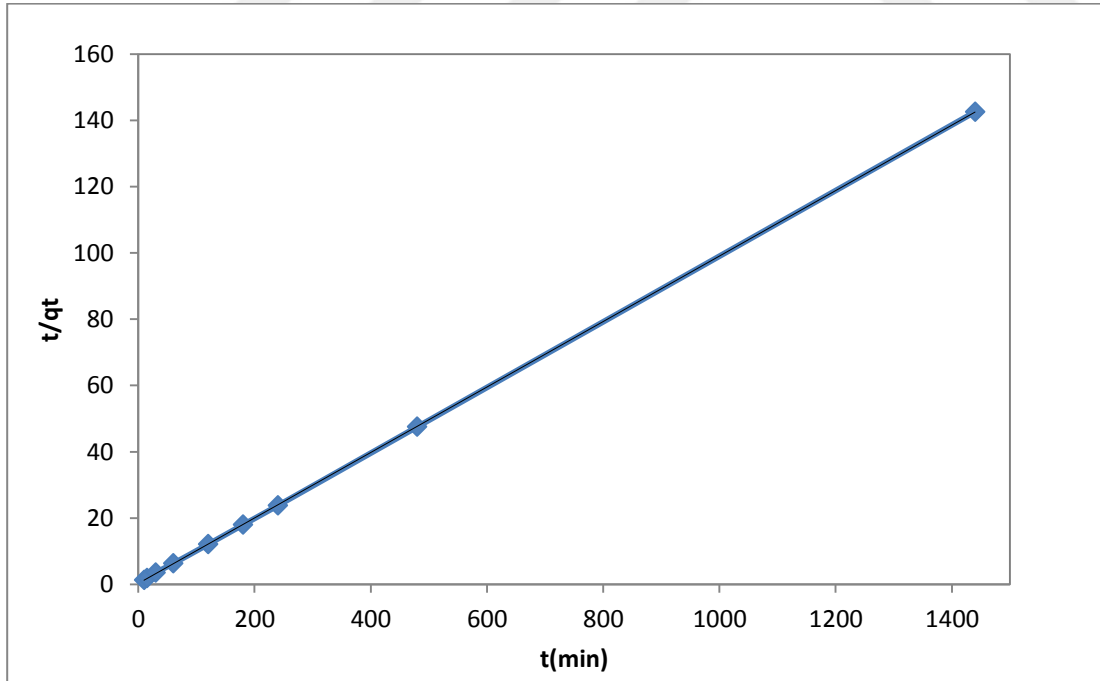


Figure 3.42 Pseudo second order plots for the sorption of Cr(VI) onto SG-A

As seen in Table 3.10, the correlation coefficients (R^2) of pseudo first order and pseudo second order model fittings were found to be 0.9726 and 0.99, respectively. These results indicated that the pseudo first order kinetics model was not suitable for Cr (VI) adsorption on SG-A. The straight lines in plot of linear pseudo-second-order equation show good agreement of experimental data with the pseudo-second order kinetic model for the initial chromium concentration of 50 ppm (mg/L). Thus the adsorption kinetics of Cr (VI) on SG-A follows the second order model. It is suggested that the Cr(VI) adsorption was involved in the chemisorption mechanism.

Diffusion-based kinetic modeling

Sorption as a heterogeneous process can be described by following steps:

- bulk diffusion toward the sorbent particle
- external mass transfer of sorbate molecules across the liquid film around the sorbent particles
- particle diffusion in the liquid contained in the pores and in the sorbate along the pore walls
- sorption and desorption within the particle and on the external surface (Ho et al., 2000)
- diffusion toward the bulk liquid

These steps can be affected by many experimental conditions, including particle size, agitation rate and pH, among others.

The intraparticle diffusion model is used to explain diffusion mechanism of adsorption process. The rate of intra-particle diffusion can be calculated according to the Weber and Morris equation (Jayakumar et al., 2014)

$$q_t = K_{id}t^{0.5} + C \quad (\text{Eq. 21})$$

where K_{id} is the intra-particle diffusion rate constant ($\text{mg} / (\text{g min}^{-0.5})$) and C is the intercept which is proportional to the boundary layer thickness. The larger C indicates the major effect of the boundary layer. If adsorption mechanism follows the intra-particle diffusion model according to Equation 19, the plot of q_t against $t^{0.5}$ should exhibit a linear relationship.

The value of rate constant of Morris–Weber transport, K_{id} , calculated from the slope of the linear plot are shown in Figure 3.43. As seen in Table 3.10, the rate constant $K_{id} = 0.3401 \text{ min}^{-1}$ was calculated from the slope of the straight line with a correlation coefficient (R^2) of 0.9475 (Jayakumar et al., 2014). Intercept value was also calculated as 6.51.

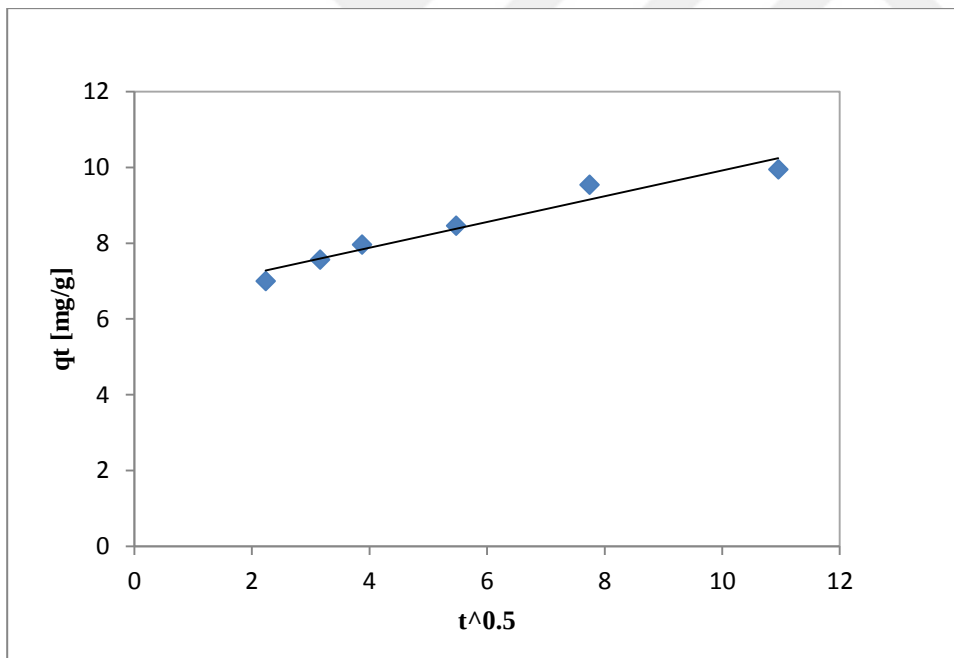


Figure 3.43 Intra particle diffusion model plots for the sorption of Cr(VI) onto SG-A.

The Elovich equation has been widely used in adsorption kinetics, which describes chemisorption mechanism in nature (Javadian et al., 2013). The Elovich

kinetic model was also used to explain the present adsorption phenomena for Cr(VI) adsorption on SG-A.

The Elovich model can be expressed as:

$$\frac{dq}{dt} = \alpha e^{-\beta q} \quad (\text{Eq. 22})$$

α as the initial adsorption rate (mg / g min) and β (g / mg) as the desorption constant. This relates the extent of the surface coverage and activation energy for chemisorption.

This equation can be simplified to above equation by considering $\alpha\beta \gg t$ and by applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad (\text{Eq. 23})$$

where q_t is the amount of gas chemisorbed at time t . As seen in Figure 3.44, a plot of q_t versus $\ln(t)$ should give a linear relationship with a slope of $(1/\beta)$ and an intercept of $(1/\beta) \ln(\alpha\beta)$. The term $1/\beta$ indicates the number of sites available for adsorption. The rate constants were $\alpha = 635.29$ and $\beta = 1.168$ with a correlation factor of 0.9752 (Javadian et al., 2013).

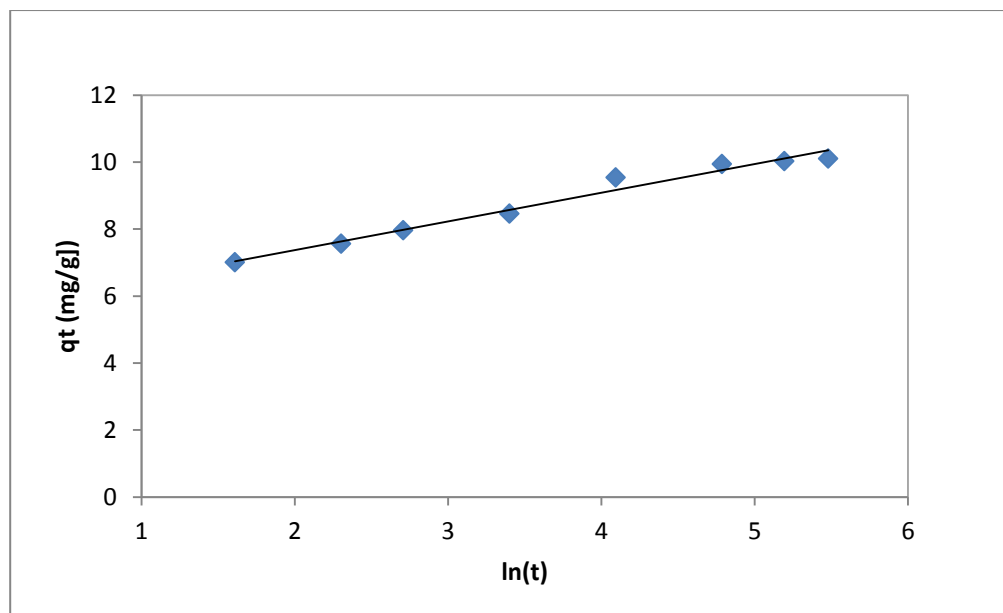


Figure 3.44 Elovich model plots for the sorption of Cr(VI) onto SG-A.

The values of the two constants (α and β) of this Elovich equation, were obtained from the slope and intercept of a plot of q_t versus $\ln(t)$, which have the good linearity as shown in Figure 3.44. It can be interpreted to understand the initial rate of the process along with the nature of sites involved in the adsorption process.

Table 3.10 Kinetic parameters obtained from various kinetic models for Cr(VI) on to SG-A adsorbent

Pseudo- First Order		Pseudo- second order		Intra- Particle diffusion		Elovich model		
k_1	R^2	k_2	R^2	K_{id}	R^2	α	β	R^2
0.0216	0.9726	0.0337	0.99	0.3401	0.9475	635.2982	1.1682	0.9752

Diffusion and reaction models

In addition, batch kinetic studies have been evaluated using diffusional and reaction models. These models include both the diffusional steps, which are bulk solution, a film layer at the external surface of the particle, pores, and the exchange reaction on the active sites.

Diffusion and reaction models describe the rate-determining steps of sorption processes regarding with ion exchange interactions. Such type of models depend on Infinite Solution Volume (ISV) and Unreacted Core Model (UC) assumptions which are developed for modeling the sorption kinetic behavior of spherical particles. Model equations are summarized in Table 3.11 (Santander et al., 2014).

Table 3.11 Summary of diffusional and reaction models

Model	Equation	Rate-determining Step
ISV	$-\ln(1 - X) = kt$ where $k = D_r \pi^2 / r_0^2$	Film diffusion
	$-\ln(1 - X^2) = K_{1i} t$ where $K_{1i} = 3DC/r_0 \delta C_r$	Particle diffusion
UCM	$X = (3C_{A0}K_{mA}/a_{r0}C_{s0})t$	Liquid film
	$3 - 3(1 - X)^{2/3} - 2X = (6D_{eR}C_{A0}/a_{r0}2C_{s0})t$	Reacted Layer
	$1 - (1 - X)^{1/3} = (k_s C_{A0}/a_{r0}C_{s0})t$	Chemical reaction

Calculated function values of fractional attainment of equilibrium (X) were plotted versus time to indicate the convenience of both diffusional and the reaction models for the sorption of Cr (VI). Kinetic behaviours of prepared adsorbent are shown in Figure 3.45 and Figure 3.46.

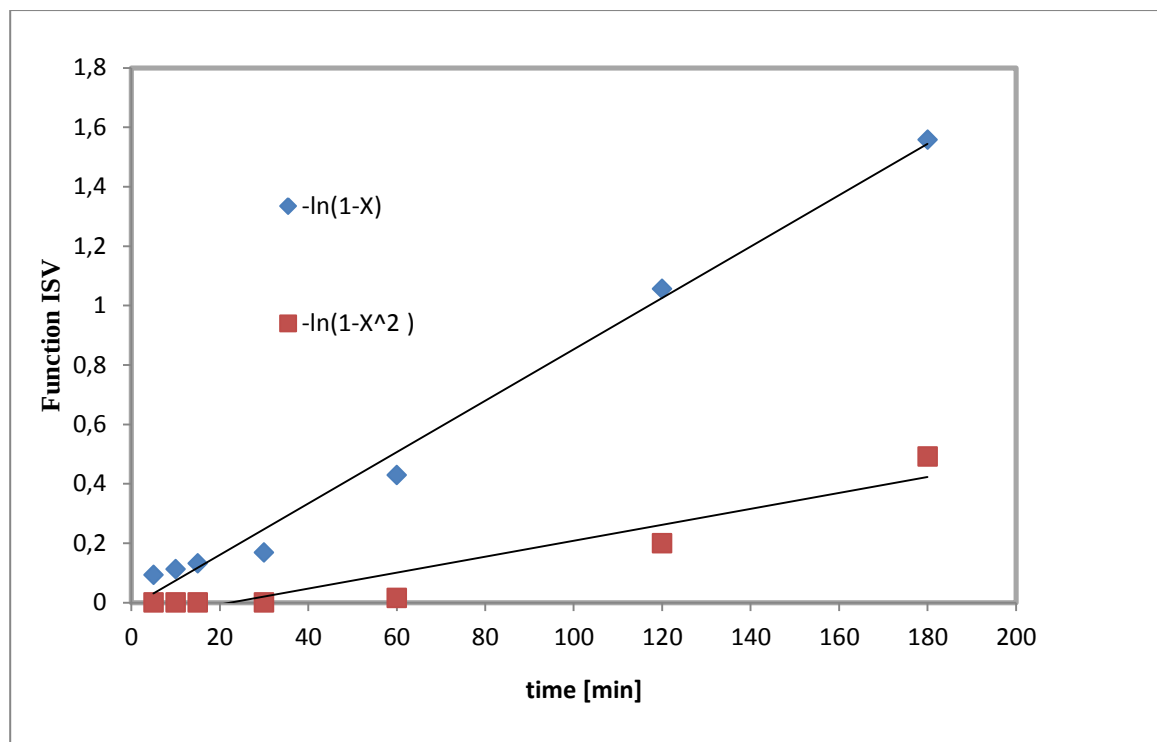


Figure 3.45 Infinite solution volume (ISV) model plots for the sorption of Cr(VI) onto SG-A.

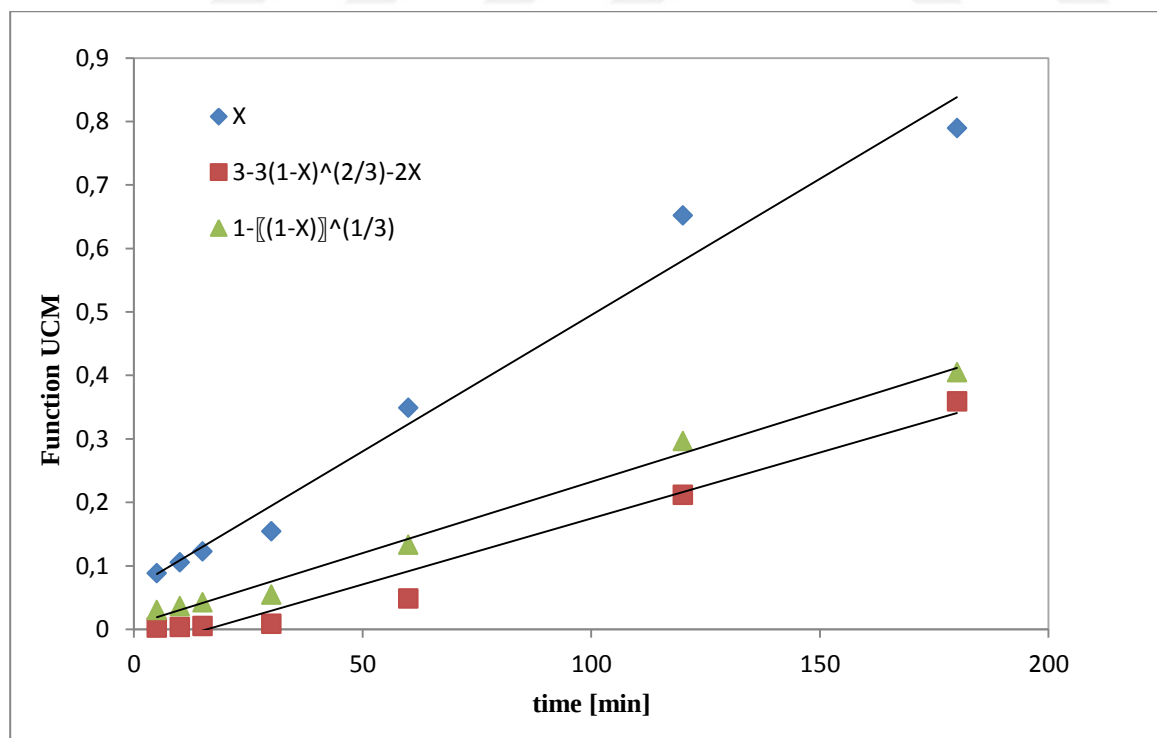


Figure 3.46 Unreacted core model (UCM) plots for the sorption of Cr(VI) onto SG-A.

Table 3.12 gives the slope values and the correlation coefficients, R^2 . As shown in the table the correlation coefficient values of the models $-\ln(1-X)$ and $1-(1-X)^{1/3}$ are greater than the minimum of the statistically meaningful R^2 , 0.874 at 99% confidence level (Lipson and Sheth, 1973).

Table 3.12 Evaluation of the kinetic models

Model	Rate-determining Step	Slope Equation	Slope	R^2
ISV	Film diffusion	$k = D_r \pi^2 / r_0^2$	0.0086	0.9906
	Particle diffusion	$K_{1i} = 3DC/r_0 \delta C_r$	0.0027	0.9044
UCM	Liquid film	$3C_{A0}K_{mA}/a_{r0}C_{s0}$	0.0043	0.9803
	Reacted Layer	$6D_{eR}C_{A0}/a_{r0}2C_{s0}$	0.0021	0.9695
	Chemical reaction	$k_s C_{A0}/a_{r0}C_{s0}$	0.0022	0.9917

These results indicate that film diffusion is the rate determining step according to infinite solution volume and the chemical reaction control with respect to unreacted core model.

Batch Mode Elution Tests

Desorption of chromium ions from SG-A adsorbent was screened by using several eluents at various concentration and constant volume in order to determine the suitable eluent and elution condition for the removal of Cr (VI) from loaded adsorbents.

As shown in Figure 3.47, the complete elutions of Cr(VI) by NaOH, NaCl, and HCl are not possible. Almost complete elution were obtained by using HNO_3 solution having the concentration of 1 M which is the most dilute one among the concentration values screened (0.1~4).

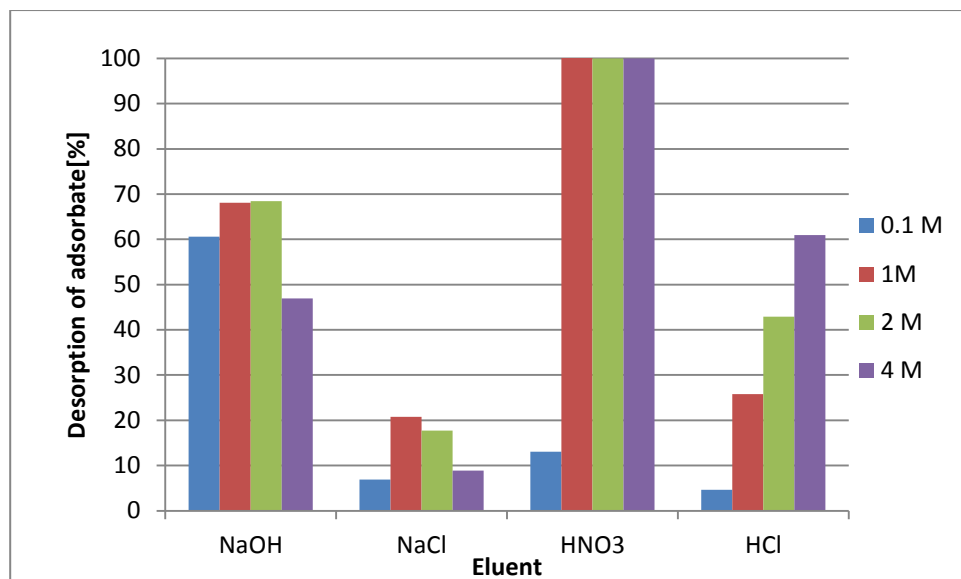


Figure 3.47 Cr(VI) stripping of performance of potential eluents.

3.2.2.2 Column Sorption Studies

These studies have been represented an attempt to assess the potential of SG-A adsorbents for the removal of Cr(VI) using fixed-bed column sorption operations. The characteristics of breakthrough curve are very important parameters for determining the operation and the dynamic conditions of an adsorption column. The column capacity at the breakthrough point can be expressed from the related Equations (9,10) given in Section A.

Figure 3.48 shows that the breakthrough curves of SG-A adsorbent for the sorption of Cr(VI) at fixed flow rate of 15 mL/min through fixed bed having the height of 6 cm. The volume of water processed (V_b) until the breakthrough point was 19.97 mL and the number of bed volumes (BV) processed at this point was 139 for the 1st cycle. The breakthrough capacity (Q_b) was found as 0.961 mg/g. It is evident from Figure 3.48 that the breakthrough curve was sharp which means that the column utilization is high.

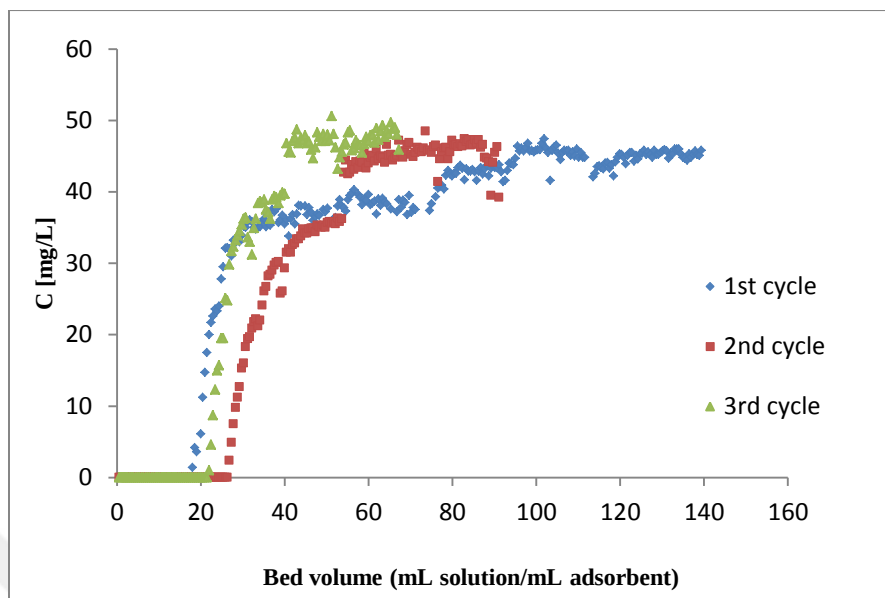


Figure 3.48 Breakthrough curve of chromium (VI) removal

In addition to these, total amount of Cr(VI) adsorbed (mg/g) and the degree of column utilization are calculated by the help of the corresponding Equations (11,12) given in Section A. The total capacity of the SG-A was determined as 2.377 mg Cr/mL-adsorbent. Corresponding utilization of the column is calculated as 40.44 (%) for for 1st cycle.

An elution test was performed as described before to evaluate the reutilization of the adsorbent. According to the previous elution studies almost complete desorption was obtained by using 1M HNO₃ as seen in Figure 3.31. Under these conditions, the elution of Cr(VI) from the adsorbed was very rapid with the elution efficiency of % 100 (see Figure 3.49).

Elution and subsequent reuse of the adsorbent is an important factor for adsorption processes. Reusability of the adsorbent can be evaluated by its adsorption performance in successive adsorption–desorption cycles. In this way, sequential adsorption–desorption experiments were carried out for three cycles in fixed bed column with a flow rate of 15 mL/min, and initial Cr(VI) concentration of 50 mg/L. Since sorption studies clarified the fact that strong acidic condition (1M HNO₃) is

necessary for the elution the Cr(VI) ions onto the bed zone. Solution of 1 M HNO₃ was used as an eluent with satisfactory results of elution efficiency (Figure 3.31). For the removal of Cr (VI), the breakthrough and total capacities of the adsorbent for each cycle are tabulated on Table 3.13. The results indicate that SG-A sorbents can be used repeatedly without significant loss of Cr(VI) adsorption capacity.

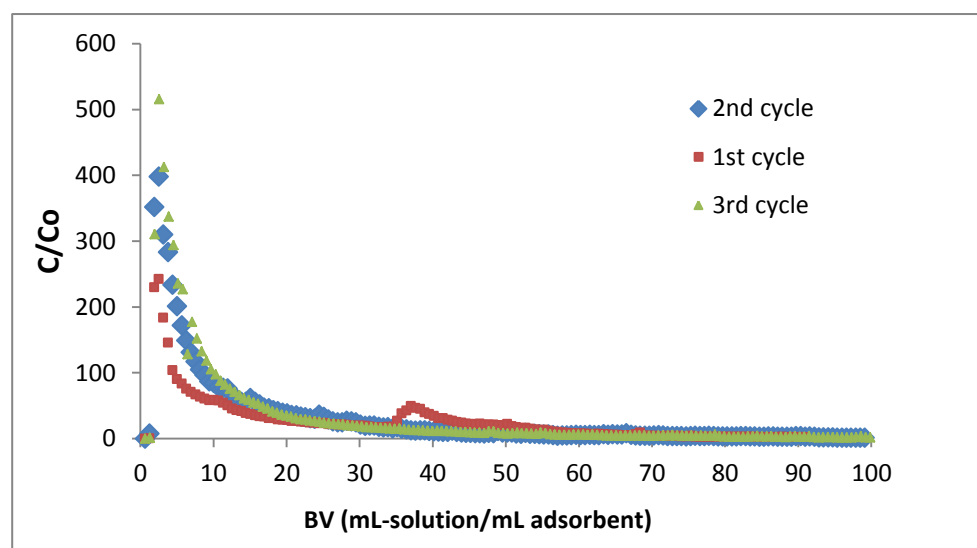


Figure 3.49 Elution profile of Cr(VI).

Table 3.13 shows that results for column study for each cycles.

Table 3.13 The results of column studies for each cycles.

	Cycle 1	Cycle 2	Cycle 3
Breakthrough point (BV)	19.970	27.280	25.820
Breakthrough capacity (mg Cr/mL-adsorbent)	0.961	1.331	1.284
BV (total)	139.340	91.108	70.640
Total capacity (mg Cr/mL-adsorbent)	2.377	2.063	1.710
Column utilization (%)	40.440	64.504	75.083
Elution efficiency (%)	71.258	100	100

4 CONCLUSION

In this work is aimed to prepare SILP materials by using various methods and investigate the potential usage of them for the sorption of Cr(VI) ions from aqueous solutions. The study includes two principle sections that examine the sorption performance of SILP adsorbents prepared by following different preparation methods.

The main conclusions derived are summarized below.

Section A:

Supported ionic liquid phase (SILP) adsorbents were **prepared by modification of nanosilica and SDVB polymeric particles with various types of ionic liquids (commercial and task specific)** in order to evaluate the Cr (VI) sorption performances. Physicochemical, morphological characterization and thermal stabilities of the prepared adsorbents were examined by using the Fourier Transform Infrared Spectrometer (FTIR), Scanning Electron Microscope (SEM), Brunauer–Emmett–Teller (BET) and Thermal Gravimetric Analysis (TGA).

FTIR spectra point out that ionic liquids have been impregnated successfully into nanoparticles and polymeric particles. The immobilization of the ionic liquid on the particles led to a pronounced and characterized change on the surface morphology. All support materials exhibited the same trend as decreasing in the surface area with increasing in the ionic liquid loading ratio. These can be concluded that ILs were placed into the pores of solid supports. In all thermal behavior characteristics of SILP, it is observed that the thermal stability of nano and polymeric particles improved with the impregnation of ionic liquids.

Then SILP materials were employed as the adsorbent for Cr(VI) sorption applications. Optimum conditions for the removal of Cr(VI) ions from aqueous solutions were determined by series of batch sorption studies. The optimum adsorbent dose was selected as 0.1 g for TT600-TS, Mox80-TS and XAD-A support

impregnated with various kind of ionic liquid with the ratio of 1:1 g-IL/g-support into 10 ml of 50 mg/L $K_2Cr_2O_7$ solution.

Among the parameters studied, pH is proved to key variable for the sorption of Cr(VI). The results show that the Cr(VI) uptake percentage of all type of SILPs has higher value at acidic pH range.

Equilibrium behaviour of nano and polymeric adsorbents fitted well with Langmuir Sorption Isotherm having the maximum adsorption capacities (q_{max}) for TT600-TS, MOX80-TS and XAD-A which are found to be 2.61, 2.25 and 8.25 mg/g, respectively.

The column mode sorption performances of silica and polymeric particles were conducted for Cr(VI) removal. They exhibited high breakthrough capacity.

All the experimental results showed that Task-Specific (TS) ionic liquid impregnated nanoparticles and polymeric supports show promising performance in the removal of Cr(VI) ions from aqueous solutions.

Section B

SILPs were prepared by sol gel method using tetraetil ortosilikat (TEOS) as precursor and using commercial and task-specific ionic liquids (tricapryl methyl ammonium chloride [A336][Cl], 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [EMIMTf2N], tricapryl methyl ammonium nitrate [A336][NO3]) to enhance the Cr(VI) sorption capacities.

FTIR, SEM, and BET surface area analyses applied to the sol-gel derived silica based adsorbents in order to characterize the adsorbents. The results make it clear that morphological and physicochemical properties of silica sorbents can be tuned by variation of IL content.

A series of batch sorption studies were conducted to investigate the sorption performances of sol-gel derived silica based adsorbents.

Cr (VI) sorption percentages achieved with silica adsorbents containing ionic liquid were higher than that of untreated adsorbents due to synergistic effect of electrostatic interaction with IL and Cr (VI) ions since SG-A type adsorbents containing tricapryl methyl ammonium chloride [A336][Cl] ionic liquid exhibited higher removal performance for Cr(VI) ions from aqueous solution, they are preferred for the further sorption studies.

Optimum operating conditions for batch sorption studies were determined as the initial pH of 4, an adsorbent dosage of 0.05 g of SG-A for 10 mL solution, and a temperature of 30 °C. A contact time of 4 hours (240 min) was found to be sufficient to achieve equilibrium.

Sorption percentages of the sol-gel adsorbents were enhanced by containing ILs up to 99 %. Equilibrium behaviour of sol-gel adsorbents fitted well with Langmuir Sorption Isotherm having the maximum adsorption capacity value of 31.74 mg/g. Sorption kinetics is well represented by pseudo-second-order models. The experimental data were better described by pseudo-second-order model as evident from correlation coefficient ($R^2=0.99$). The infinite solution volume (ISV) model and unreacted core model (UCM) plots for the sorption of Cr(VI) onto SG-A were also investigated, respectively. According to results of diffusion and reaction models, it can be concluded that the rate is controlled by either film diffusion process or the chemical reaction during the sorption process.

The thermodynamic parameters like standard Gibb's free energy (ΔG^0), standard enthalpy (ΔH^0) and standard entropy (ΔS^0) were investigated for predicting the nature of adsorption. The calculated thermodynamic parameters indicated that endothermic and spontaneous nature of the adsorption process under studied conditions.

Desorption of Cr (VI) from SG-A has been studied using 1 M HNO_3 , maximum desorption efficiency was almost 100%. The adsorption-desorption cycle

results indicate that SG-A sorbents can be used repeatedly without significant loss of Cr(VI) adsorption capacity.

Sorption of Cr(VI) ions from aqueous solution by sol-gel silica based adsorbents containing Aliquat 336 takes place favorably and these type of adsorbents are promising agents in the adsorption.



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CURRICULUM VITAE

Personal Information:

Name – Surname: Merve ARABACI

Nationality: Turkish

Birth Date and Place : 30.10.1990 – Balıkesir / Turkey

Driving licence: B

Contact Information:

Address: Hasan Basri Çantay Mah Çicek Sok. No:11 Kat:4 Altıeylül/ Balıkesir

Mobile Phone : +90(537) 702-38-30

E-mail : mmerve.arabaci@gmail.com

Education:

2014-2018

Master Degree

Ege University, Graduate School of Applied and Natural Sciences, Chemical Engineering Department

Master Thesis:

Preparation, Characterization and Sorption Performance of Supported Ionic Liquid Phase (SILP) Systems

Supervisor: Assist. Prof. Dr. Nilay GIZLI

2009-2014

Bachelor Degree

Ege University, Engineering Faculty, Chemical Engineering Department

Diploma Project:

Oxidation of Phenolic Compounds by Heterogeneous photoFenton-Like Oxidation Over Iron Containing TiO₂ Catalysts in the Presence and Absence of Ultrasound

Supervisor: Prof. Dr. Gonul GUNDUZ

Qualifications:**Computer Skills:**

MS Office (Word/ Excel/ Powerpoint), IntelliCAD2000, Matlab

Foreign Languages:

English Upper Intermediate

German Beginner

Projects:

- TUBITAK (Turkish Scientific and Research Council) project with the contact no: 213M537 as a scholarship student.
- BAP (Bilimsel Arastirma Projeleri) "Destekli iyonik sivi faz sistemleri (SILP) ile Metal iyonlarnin uzaklastirilmesi 15 MUH 005 as a researcher

Training Period:

- ECZACIBAŞI Holding Co.(VitrA Karo), Istanbul (Turkey), 2013 (1 month)
- TURYAĞ Food Inc Co., Balikesir (Turkey), 2012 (1 month)

Work Experience:

- VESTEL WHITE GOODS Manisa (Turkey)
Research and Development Department, Raw Materials & Paint Specialist
(2016-Present)