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

**(MASTER OF SCIENCE THESIS)**

# PREPARATION OF SOLVENT IMPREGNATED RESINS FROM VARIOUS POLYMERIC ADSORBENTS AND THEIR UTILIZATION FOR REMOVAL OF Cr(VI) IONS FROM AQUEOUS SOLUTIONS

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# ÖZET

## ÇEŞİTLİ POLİMERİK ADSORBANLARDAN ÇÖZÜCÜ EMDİRİLMİŞ REÇİNELERİN HAZIRLANMASI VE BU REÇİNELERİN SULU ÇÖZELTİLERDEN Cr(VI) İYONLARININ GİDERİMİNDE KULLANILMASI

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Su yaşam döngüsü için çok önemlidir. Ancak günümüzde özellikle ağır metal içeren endüstriyel atık sular nedeniyle su kaynakları kirlenmektedir. Bu ağır metal kirlilik kaynaklarından bir tanesi Cr(VI) iyonudur. Polimerik adsorbanlara çeşitli ekstraksiyon reaktifleri emdirilerek elde edilen çözücü emdirilmiş reçineler Cr(VI) iyonlarının gideriminde kullanılan yeni ve etkili malzemelerdir.

Bu çalışmada, sıvı iyon değiştirici olarak trioktilmetilamonyum klorür (Aliquat 336), polimerik adsorban olarak Diaion HP 20 ve Diaion HP 2MG reçineleri kullanılmıştır. Çözücü emdirilmiş reçineler 1 g Aliquat 336/g-reçine, 2 g Aliquat 336/g-reçine ve 3 g Aliquat 336/g-reçine emdirme oranlarında hazırlanmıştır.

Elde edilen çözücü emdirilmiş reçineler model çözeltilerden Cr(VI) iyonlarının gideriminde kullanılmıştır. Bu amaçla kesikli ve kolon çalışmaları yapılmış, kesikli çalışmalarda elde edilen sonuçlar, Langmuir ve Freundlich adsorpsiyon modellerine uygulanmıştır. Ayrıca Cr(VI) sorpsiyonunun kinetik olarak tepkime derecesi ve hız tayin basamağının belirlenmesi için bazı matematiksel modeller kullanılmıştır.

Ayrıca, Şili'de bulunan Concepcion Üniversitesinde kuaterner amonyum grubu içeren poli[(Ar-vinilbenzil) trimetil amonyum klorür] P(ClVBTA) ve poli[(3-Akrilamidopropil) trimetil amonyum klorür] P(ClAPTA) reçineleri sentezlenmiş ve bu reçinelerin Cr(VI) giderim performansları ticari Amberlite IRA-400 reçinesi ile karşılaştırılmıştır.

P(ClVBTA), P(ClAPTA) ve Amberlite IRA-400 reçineleri ile Cr(VI) giderimine pH'ın etkisi incelenmiş, farklı sıcaklıklarda denge çalışmaları gerçekleştirilerek sıcaklığın Cr(VI) giderimine etkisi incelenmiştir. Bu çalışmada elde edilen veriler Langmuir ve Freundlich adsorpsiyon izoterm modellerine uygulanmıştır. Ayrıca reçinelerin Cr(VI) sorpsiyonuna ilişkin hız mertebesi ve hız tayin basamağının belirlenmesi için bazı matematiksel modeller kullanılmıştır.

Çalışmalar sonucunda, çözücü emdirilmiş reçineler ve sentezlenen iyon değiştirici reçinelerin Cr(VI) giderimine uygun olduğu saptanmıştır. Çözücü emdirilmiş reçinelerin Cr(VI) giderim performaslarının emdirme oranı arttıkça yükseldiği ve HP 20 bazlı çözücü emdirilmiş reçinelerin kapasitelerininin aynı impregnasyon oranlarında hazırlanan HP 2MG bazlı çözücü emdirilmiş reçinelerden daha iyi olduğu gözlenmiştir. İyon değiştirici reçinelerin Cr(VI) giderim performanslarının ise P(ClAPTA) > P(ClVBTA) > Amberlite IRA-400 sıralamasında olduğu gözlenmiştir.

**Anahtar sözcükler:** Aliquat 336, Çözücü emdirilmiş reçine, Cr(VI), iyon değiştirme, kesikli çalışma, kolon çalışması.

# ABSTRACT

## PREPARATION OF SOLVENT IMPREGNATED RESINS FROM VARIOUS POLYMERIC ADSORBENTS AND THEIR UTILIZATION FOR REMOVAL OF Cr(VI) IONS FROM AQUEOUS SOLUTIONS

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Water is essential for life cycle. However, nowadays water sources are polluted because of industrial waste waters especially including heavy metals. Cr(VI) is one of the pollution sources. Solvent impregnated resins (SIRs) are efficient and innovative materials for using removal of Cr(VI).

In this study, trioctylmetylammonium chloride (Aliquat 336), Diaion HP 20 and Diaion HP 2MG were used as a liquid ion exchanger and polymeric adsorbents, respectively. Solvent impregnated resins were prepared in the impregnation ratios of 1 g Aliquat 336/g-resin, 2 g Aliquat 336/g-resin ve 3 g Aliquat 336/g-resin.

Obtained solvent impregnated resins were used for removal of Cr(VI) ions from model solutions. For this purpose, batch and column studies were investigated. Langmuir and Freundlich adsorption models and mathematical models were applied using data of batch studies. Also some mathematical modeling study was performed to investigate the rate order and rate determining step of Cr(VI) sorption.

Poly[(Ar-vinylbenzyl) trimethyl ammonium chloride] P(ClVBTA) and poly[(3-Acrylamidopropyl) trimethyl ammonium chloride] P(ClAPTA) resins containing quaternary ammonium groups were synthesized at University of Concepcion and performance of these resins for Cr(VI) removal was compared with that of commercial Amberlite IRA-400 resin.

Effect of pH on performance of Cr(VI) removal was investigated by P(ClVBTA), P(ClAPTA) and Amberlite IRA-400 resins. Equilibrium studies were performed at different temperatures and the effect of temperature on Cr(VI) sorption was investigated. Langmuir and Freundlich adsorption models were applied using data of equilibrium study. Also some mathematical modeling study was performed to investigate the rate order and rate determining step of Cr(VI) sorption.

Results of studies showed that solvent impregnated resins and synthesized ion exchange resins are suitible for Cr(VI) removal. It was observed that Cr(VI) removal performance of solvent impregnated resins increased when impregnation ratio increased and capacity of HP 20 based solvent impregnated resins were better than HP 2MG based SIR. Cr(VI) removal performance of ion exchange resins increased in an order of P(ClAPTA) > P(ClVBTA) > Amberlite IRA-400.

**Key words:** Aliquat 336, Cr(VI), batch study, column study, ion exchange, solvent impregnated resins.

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# NOMENCLATURE

| Symbol | Explanation |
|---|---|
| C | concentration of the solute in water (mg/L) |
| $C_0$ | initial concentration of the solute in water (mg/L) |
| $C_e$ | equilibrium concentration (mg/L) |
| $q_e$ | amount of Cr(VI) sorbed at equilibrium (mg/g) |
| $q_t$ | amount of Cr(VI) sorbed at time t (mg/g) |
| b | Langmuir constant |
| $k_F$ | Freundlich constant |
| n | dimensionless variable indicative of favourability of sorption |
| $k_1$ | rate constant of pseudo first-order sorption ($min^{-1}$) |
| $k_2$ | rate constant of pseudo second-order sorption (g/mg min) |
| t | time |
| a | stoichiometric coefficient |
| C | total concentration of both exchanging species (M) |
| $C_{Ao}$ | concentration of species A in bulk solution (M) |
| D | diffusion coefficient in solution phase ($m^2/s$) |
| $D_r$ | diffusion coefficient in solid phase ($m^2/s$) |
| $D_{eR}$ | effective diffusion coefficient in solid phase ($m^2/s$) |
| $k_s$ | reaction constant based on surface (m/s) |

## NOMENCLATURE (continued)

| Symbol | Explanation |
|---|---|
| $K_{mA}$ | mass transfer coefficient of species A through the liquid film (m/s) |
| K | rate constant (L/s) |
| $r_o$ | average particle radius (mm) |
| X | fractional attainment of equilibrium or extent of resin conversion |
| $\delta$ | film thickness (mm) |

Abbreviations

| | |
|---|---|
| EAWAG | Swiss Federal Institute of Environmental Science and Technology |
| SANDEC | Department of Water and Sanitation in Developing Countries |
| US EPA | United States Environmental Protection Agency |
| OSHA | Occupational Safety and Health Administration |
| RO | reverse osmosis |
| UF | ultra filtration |
| NF | nano filtration |
| MF | micro filtration |
| ED | electrodialysis |
| IX | ion exchange |

# 1. INTRODUCTION

## 1.1 Water Treatment

Water covers approximately 75 percent of our world's surface, representing a volume of over one billion cubic kilometers. Water and life are intricately linked. Water makes up about 70 percent of our bodies. More than half of the world's species of plants and animals live in water, and even our terrestrial-derived food is totally dependent on and often largely composed of water (Smol, 2002). So, water is essential for our life in adequate amount and good quality (EAWAG-SANDEC, 2002). However, only a very small portion of this water is fresh and accessible (Smol, 2002).

The pollution of rivers and streams with chemical contaminants is one of the most crucial environmental problems (Sonune and Ghate, 2004). A large volume of effluents with hazardous species, namely heavy metals and semi-metals, is being discharged every day from industries into aquatic systems (Chowdhury et al., 2012). They may also enter the water indirectly through the use of plant health products, such as biocides and fertilizers, in agriculture. In general, water-soluble substances can be transported and distributed more easily in the water cycle. Discharge resulting from lax enforcement of the rules, illegal use and inappropriate application of substances may be considerable (Oller et al., 2011). A number of chemical contaminants —including DDT, dioxins, polychlorinated biphenyls (PCBs), and heavy metals— are associated with conditions ranging from skin rashes to various cancers and birth defects. Besides affecting human health, water pollution has adverse effects on ecosystems (Calhoun, 2005).

The pollution of water has been a matter of serious concern over worldwide for the last few decades (Chowdhury et al., 2012). An increasing demand for fresh water along with the larger amounts of wastewater generation due to increase in the world population and development of industrial applications make the recycling of the waste waters an imperative issue (Polat and Erdogan, 2007).

### 1.1.1. Removal of heavy metals from water

Heavy metal contamination is a common, important, and growing problem around the world (Mulligan et al., 2009). Waste effluents containing metals such

as copper, nickel, zinc, chromium, cadmium, aluminum, silver, gold, etc. arise mainly from manufacturing processes such as electroplating, semiconductor and electronics, metal finishing, and leather industries (Kabay et al., 2004a). The amount of heavy metals is high in the industrial wastewaters and removal of them is one of critical importance due to their high toxicity or carcinogenic effect and tendency to accumulate in living organisms and heavy metals in industrial waste water endanger the environment if discharged without adequate treatment (Polat and Erdogan, 2007; Prados and Gutiérrez-Cervelló, 2011). Especially chromium, one of the most toxic heavy metals in the environment, has gradually been increased predominantly by industrial activities such as numerous industrial processes that include galvanization, steel, paints, textiles, oxidative dyeing, cooling water towers, leather tanning, corrosion control, electroplating and batteries (Kabay et al., 2004a; Hosseini-Bandegharei et al., 2010; Alpaydın et al., 2011).

Chromium is an odorless and tasteless metallic element. It is found naturally in rocks, plants, soil and volcanic dust, and animals. The most common forms of chromium that occur in natural waters in the environment are trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)). (US EPA, 2008). Cr(III) is not a significant groundwater contaminant whereas Cr(VI) is approximately 100 times more toxic than Cr(III) (Kabay et al., 2003). Chromium (VI) can be toxic as it can diffuse as $CrO_4^{2-}$ or $HCrO_4^-$ through cell membranes and oxidize biological molecules (Hosseini-Bandegharei et al., 2010).

Breathing in high levels of Cr(VI) can cause irritation to the nose and throat. Chromate compounds can cause asthma symptoms such as wheezing and shortness of breath. Cr(VI) can cause an allergic reaction on skin called allergic contact dermatitis (OSHA DSG, 7/2006) and Cr(VI) is known to exhibit carcinogenic properties; attacks liver, kidney and lungs. And when Cr(VI) is ingested higher than its permissible level, it causes health disorders; such as vomiting and hemorrhage (Qureshi et al., 2009).

It is necessary to understand the solution chemistry of hexavalent chromium in order to explain the binding mechanism of chromate by various adsorbents or ion exchange materials. The distribution of Cr(VI) species is dependent on both the total concentration of Cr(VI) and pH of the equilibrium solution. Chromium exists in five main forms in aqueous solution. The reactions between these species

and the reaction equilibrium constants (K) are shown in Eqs. 1.1–1.4 (Saha et al., 2004).

$$H_2CrO_4 \leftrightarrow H^+ + HCrO_4^- \quad K_1 = 1.21 \tag{1.1}$$

$$HCrO_4^- \leftrightarrow H^+ + CrO_4^{2-} \quad K_2 = 3.0 \times 10^{-7} \tag{1.2}$$

$$2HCrO_4^- \leftrightarrow Cr_2O_7^{2-} + H_2O \quad K_3 = 35.5 \tag{1.3}$$

$$HCr_2O_7^- \leftrightarrow H^+ + Cr_2O_7^{2-} \quad K_4 = 0.85 \tag{1.4}$$

A speciation diagram showing the relative distribution of different Cr(VI) species in water as a function of pH and total chromate concentrations of 0.001 M and below are shown in Figure 1.1 (Saha et al., 2004).

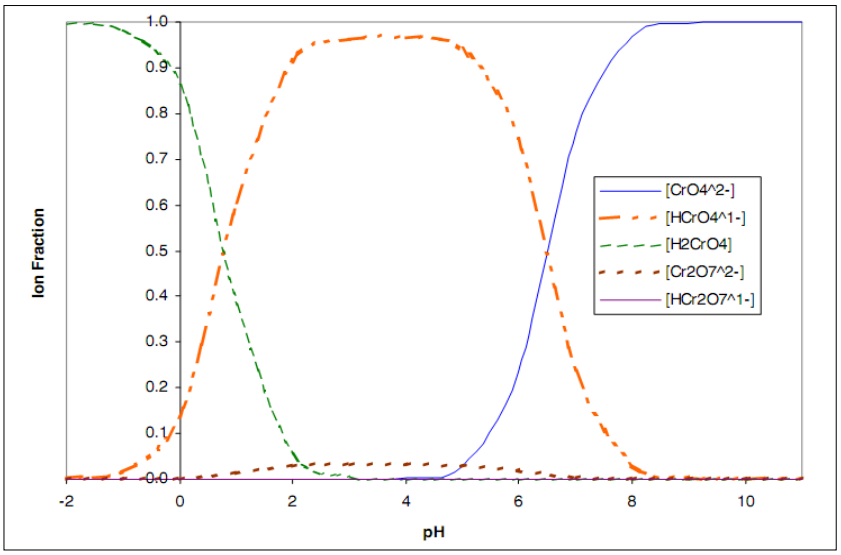


**Figure 1.1.** Cr(VI) speciation, total concentration 0.001 M (Saha et al., 2004).

Several treatment technologies have been developed for eliminating heavy metals from wastewater in recent years (Fonseca et al., 2006). Besides, use of effective wastewater treatment technologies allows the industrial facilities to create water recycling systems, saving discharge fees and freshwater supply payment (Prados and Gutiérrez-Cervelló, 2011).

The heavy metal removal and recovery processes include the following techniques:

– Precipitation.

– Adsorption and biosorption.

– Coagulation and flocculation.

– Electrochemical treatment (Prados and Gutiérrez-Cervelló, 2011).

## Precipitation

Chemical precipitation is effective and by far the most widely used process in industry because it is relatively simple and inexpensive to operate. In precipitation processes, chemicals react with heavy metal ions to form insoluble precipitates. The forming precipitates can be separated from the water by sedimentation or filtration. And the treated water is then decanted and appropriately discharged or reused. The conventional chemical precipitation processes include hydroxide precipitation and sulfide precipitation (Fu and Wang, 2011). However, precipitation is less effective for the removal of toxic metals at low concentrations that are above the recommended discharge limits. Under these circumstances, further treatment is necessary prior to waste disposal (Kabay et al., 2004a).

Gheju and Balcu (2011) investigated the total removal of Cr(VI) from Cr(VI) aqueous solutions by reduction with scrap iron and subsequent precipitation of the resulted cations with NaOH. In that study Cr(VI) solution was passed through the column that was packed with scrap iron. Maximum removal efficiency of the Cr(total) achieved in the clarifier under circumneutral and alkaline (pH 9.1) conditions was 98.5%.

Golder et al. (2011) reported aqueous Cr(VI) reduction/removal by electrotreatment with mild steel electrode in a batch stirred reactor. Cr(VI) removal is due to simultaneous reduction to Cr(III) followed by precipitation and adsorption of Cr(VI) on $Fe(OH)_3(s)/Cr(OH)_3(s)$ sludge formed. They showed that acidic pH favors Cr(VI) reduction to Cr(III) where as neutral conditions is effective for $Cr(OH)_3(s)/Fe(OH)_3(s)$ precipitation in a combined electrocoagulation–electroflotation reactor using mild steel electrode.

## Adsorption and biosorption

Adsorption is now recognized as an effective and economic method for heavy metal removal from wastewater treatment. The adsorption process offers flexibility in design and operation and in many cases will produce high-quality treated effluent. In addition, because adsorption is sometimes reversible,

adsorbents can be regenerated by suitable desorption process (Fu and Wang, 2011). However, in the most cases, the use of adsorbents requires an effluent neutralization step. Indeed, the neutralization of acid effluents must take place to allow their disposal in sewerage systems (Prados and Gutiérrez-Cervelló, 2011).

Biosorption of heavy metals from aqueous solutions is a relatively new process that has been confirmed a very promising process in the removal of heavy metal contaminants. The major advantages of biosorption are its high effectiveness in reducing the heavy metal ions and the use of inexpensive biosorbents. Biosorption processes are particularly suitable to treat dilute heavy metal wastewater (Fu and Wang, 2011). It implies the use of alive or dead biomass and their derivatives. Many studies have been carried out for the adsorption of heavy metals on various types of biomass (bacteria, yeasts, fungi, freshwater algae) (Prados and Gutiérrez-Cervelló, 2011).

Natale et al. (2007) studied removal of chromium ions in aqueous solution by granular activated carbon (GAC) and char of South African coal (CSAC). They reported that chromium adsorption mainly depends on the availability of chromium ions in solution and on the occurrence of redox reactions between the surface groups and the Cr(VI) which lead to the formation of Cr(III).

Levankumar et al. (2009) investigated batch removal of Cr(VI) from aqueous solutions by Ocimum americanum L. seed pods. It was capable of removing 100% of chromium from the aqueous solutions.

Wei et al. (2009) also examined the selective adsorption of Cr (VI) from the wastewater of Cr (VI)–Ni (II) by magnetically iron–nickel oxide. They reported that synthetic iron–nickel oxide magnetic particle in co-sedimentation was suitable for selective adsorbing and recycling hexavalent chromium from the binary Cr (VI) and Ni (II) liquid in wastewater.

## Coagulation and flocculation

Coagulants and flocculants enhance dissolved metal removal and reduce sludge volume during conventional acidic drainage and high-density sludge treatment. Coagulants and flocculants are chemicals that can be added during acidic drainage treatment (Prados and Gutiérrez-Cervelló, 2011). Coagulation is the destabilization of colloids by neutralizing the forces that keep them apart.

Many coagulants are widely used in the conventional wastewater treatment processes such as aluminium, ferrous sulfate and ferric chloride, resulting in the effective removal of wastewater particulates and impurities by charge neutralization of particles and by enmeshment of the impurities on the formed amorphous metal hydroxide precipitates. Also, coagulation is one of the most important methods for wastewater treatment, but the main objects of coagulation are only the hydrophobic colloids and suspended particles (Fu and Wang, 2011).

Flocculation is the action of polymers to form bridges between the flocs and bind the particles into large agglomerates or clumps. Once suspended particles are flocculated into larger particles, they can usually be removed or separated by filtration, straining or floatation. Today many kinds of flocculants, such as PAC, polyferric sulfate (PFS) and polyacrylamide (PAM), are widely used in the treatment of wastewater (Fu and Wang, 2011).

Song et al. (2004) studied to develop a treatment system that can effectively reduce the concentration of pollutants in tannery wastewater to environmentally acceptable levels. Aluminium sulphate and ferric chloride were used as a coagulant in the process. They achieved 74-99% chromium (at an initial concentration of 12 mg/L) removal using the optimum coagulant dosage (800 mg/L) in the optimum pH range (around 7.5).

## Electrochemical treatment

Electrochemical methods involve the plating-out of metal ions on a cathode surface and can recover metals in the elemental metal state. Electrochemical wastewater technologies involve relatively large capital investment and the expensive electricity supply, so they have not been widely applied. However, with the stringent environmental regulations regarding the wastewater discharge, electrochemical technologies have regained their importance worldwide during the past two decades (Fu and Wang, 2011).

Electrochemical heavy metal wastewater treatment techniques are regarded as rapid and well-controlled that require fewer chemicals, provide good reduction yields and produce less sludge. However, electrochemical technologies involving high initial capital investment and the expensive electricity supply, this restricts its development (Fu and Wang, 2011).

Rana et al. (2004) investigated determine the feasibility of electrochemical removal of chromium ions from industrial wastewater using carbon aerogel electrodes as a function of pH, concentration and charge. They reported that the removal is strongly pH dependent and the carbon aerogel electrode was suitable for the chromium removal because of its unique characteristics. In this study 98.5% Cr(VI) removal was obtained under high charge (0.8A h) and acidic conditions (pH 2).

Heidmann and Calmano (2008) investigated the performance of an electrocoagulation (EC) system for removing $Zn^{2+}$, $Cu^{2+}$, $Ni^{2+}$, $Ag^{+}$ and $Cr_2O_7^{2-}$ with aluminium electrodes.

Ölmez (2009) examined the performance of EC to remove Cr(VI) having a high concentration of 1470 mg/L. 7.4 amper of applied electric current, 33.6 mM electrolyte (NaCl) concentration and 70 min of application time were indicated as the optimum conditions for 100% Cr(VI) removal.

Tian et al. (2012) studied on removal of Cr(VI) by electroreduction. In this study, they used stainless steel (SS) and polypyrrole (ppy) modified electrode for reduction of Cr(VI) to Cr(III). They obtained 92% of Cr(VI) removal with ppy modified electrode.

## Solvent extraction

Solvent extraction is one of the most efficient methods of concentrating and separating different metal species from aqueous solutions (Wionczyk et al., 2006). This technique was used for many years for a broad range of separations in hydrometallurgy (Prados and Gutiérrez-Cervelló, 2011). It is possible to separate and preconcentrate metals as value added products from solutions in the presence of complexing anionic species (Kumar et al., 2010; Shukla and Rao, 2002).

Separation is carried out in contact with immiscible organic phase to form salts or complex compounds which give a favorable solubility distribution between the aqueous and organic phases (Prados and Gutiérrez-Cervelló, 2011). Chelating ligands like diketones, oxines, oximes, amides, thiothenoyltrifluoroacetone, dithiocarbamates and their derivatives with donor set [O, O]−, [O, N]−, [O, S]− and [S, S]− have been extensively used for this purpose (Kumar et al., 2010; Shukla and Rao, 2002).

The major drawback of solvent extraction is the loss of extractant / solvent in large-scale industrial applications. The small but finite aqueous solubility of extractants, diluents and modifiers is a major disadvantage of solvent extraction. This not only adds to the cost of the process, through loss of reagents, but may also contaminate effluents with hazardous organics. The loss of organics by evaporation and entrainment is also a potential problem. Moreover, solvent extraction is inefficient at trace metal ion concentrations because of excess solvent requirement (Kabay et al., 2003). Another difficulty of the solvent extraction technique is the recovery of the extracted ion from the organic phase. This process, called stripping, follows the extraction step. The search for suitable stripping reaction and operation conditions is not always successful. As a result, the solvent extraction systems are often designed to improve the separation efficiency in benefit of the stripping procedure (Zagorodni, 2007).

Senol (2004) investigated extraction of Cr(VI) from the aqueous acidic solution into a co-existing organic phase containing Alamine 336 ($C_8$–$C_{10}$ tertiary amine mixture) and diluent (xylene). Additionally a comparative study of the extraction degrees of Cr(VI) by Alamine 336 and Aliquat 336 extractants for the pH range of 1–7 was evaluated. The extraction degree of Cr(VI) by Aliquat 336 remains almost 100% between pH at 2 and 4.5. By Alamine 336 system, extraction degree of Cr(VI) was 90% at high acidic region.

Venkateswaran and Palanivelu (2004) examined the extraction of Cr(VI) from aqueous solutions by tetrabutyl ammonium bromide (TBAB) salt in dichloromethane. The maximum extraction efficiency of Cr(VI) was obtained at pH 1 ± 0.1 and 500 mg TBAB/10mL of dichloromethane as 96% Cr(VI) extraction. They used 0.1 M sodium hydroxide for stripping Cr(VI) from the loaded solvent. Cr(VI) was completely stripped.

Agrawal et al. (2008) investigated extractive removal of Cr(VI) from chloride solutions using Cyanex 923 mixed with kerosene. Under the optimum experimental conditions 98.6–99.9% of Cr(VI) was extracted in 3–5 min at O/A of 2 with the initial feed concentration of 1 g/L of Cr(VI).

### 1.1.2 Innovative methods for metal removal from water

#### 1.1.2.1 Ion exchange

The range of application of the ion exchange method was remarkably extended. All over the world industry is forced to diminish down to acceptable level contents of heavy metal in water and industrial wastewaters (Dabrowski et al., 2004). The present areas of application are mainly in the treatment of obnoxious effluents from the metal fabrication industries and radioactive liquid streams where economic benefits result from recovering reagents and recovering clean water (Harland, 1994). Ion exchange processes have been widely used to remove heavy metals from wastewater due to their many advantages, such as high treatment capacity, high removal efficiency and fast kinetics (Fu and Wang, 2011). Clearly, ion exchange methods can overcome what would otherwise be a difficult waste disposal problem, and the bonuses of recovering reagents and process water are valuable economically (Harland, 1994).

Tenório and Espinosa (2001) investigated efficiency of two column systems for wastewaters containing chromates that were taken from rinse tanks of chromium plating companies. One of the systems was composed of the strongly acidic cation exchanger Amberlite IR-120 Na (gel type of polystyrene divinylbenzene skeleton) and of the strongly basic anion exchanger Amberlite IRA-420 (gel type and polystyrenedivinylbenzene skeleton) (System 1) and the other of the cation exchanger Amberlite IR-120 Na on the weakly basic anion exchanger Amberlite IR-67RF (gel type and acrylate skeleton) (System 2). They found that system 2 was gave the best result but system 1 presented problems in elution of retained chromium.

Rengaraj et al. (2001) examined Cr(III) removal from water. They used IRN77 and SKN1 cation exchange resins for this purpose. These resins removed the Cr(III) extent of 98% at the solution pH. The adsorption process obeys the Freundlich adsorption isotherm. The efficiency of these resins towards the removal of chromium from synthetic chromium solution alone is higher than that of synthetic coolant water.

Cavaco et al. (2007) studied on performance of commercial ion exchange resins for removing chromium trivalent from industrial effluents using a chelating exchange resin (Diaion CR11) and a weak cationic resin (Amberlite IRC86). The

chromium solutions employed in the experiments were synthetic solutions and industrial effluents.

Shi et al. (2009) performed removal of hexavalent chromium from electroplating industry wastewater by anion-exchange resins D301, D314 and D354. They found the maximum removal of Cr(VI) in the pH range of 1–5.

Neagu and Mikhalovsky (2010), studied on removal of hexavalent chromium from aqueous solution by ion exchange resins. In that study, they synthesized quaternized crosslinked poly(4-vinylpyridines) by nucleophilic substitution reaction of 4-VP:DVB copolymers of gel and porous type with benzyl chloride (PyR1) and 2-chloracetone (PyR2) as halogenated compounds and compared their capacity with commercial resin Amberlite IRA-400. They found that PyR1 and PyR2 resins exhibited good values of the ion exchange capacity in comparison with the commercial strong base anion exchange resin, Amberlite IRA-400 and pyridine resins exhibited the higher selectivity for Cr(VI) in the presence of sulfate anions than commercial Amberlite IRA-400.

Edebali and Pehlivan (2010) investigated the removal of Cr(VI) from aqueous solution by two commercially available resins (Amberlite IRA96 and Dowex 1×8). The optimum pH for Cr(VI) adsorption was found as 3.0 for these resins.

### 1.1.2.2 Membrane processes

In recent years, membranes and membrane separation techniques have grown from a simple laboratory tool to an industrial process with considerable technical and commercial impact (Porter, 1990). Membrane technology is considered as one of the most effective processes for water and wastewater treatment. It is a compact system, economically feasible and has high rejection level of pollutants. Membrane technology has been given special focus in water treatment processes because of its capability in removing physical and chemical matters at a higher-degree of purification. Membrane technologies are various and considered as proper methods. Membrane technology is presently an established industrial process which can be found in all industrial areas (Prados and Gutiérrez-Cervelló, 2011) which cover water and dairy purification, sea and brackish water desalination, wastewater reclamation, food and beverage production, gas and vapor separation, energy conversion and storage, air pollution

control and hazardous industrial waste treatment, hemodialysis, proteins and microorganisms separation, etc. (Wang et al., 2011).

In association with separation, concentration or purification processes, a membrane can be essentially defined as a barrier to separate two phases and be able to restrict the transport of various components in a selective manner, as shown schematically in Fig. 1.2. (Wang et al., 2011).

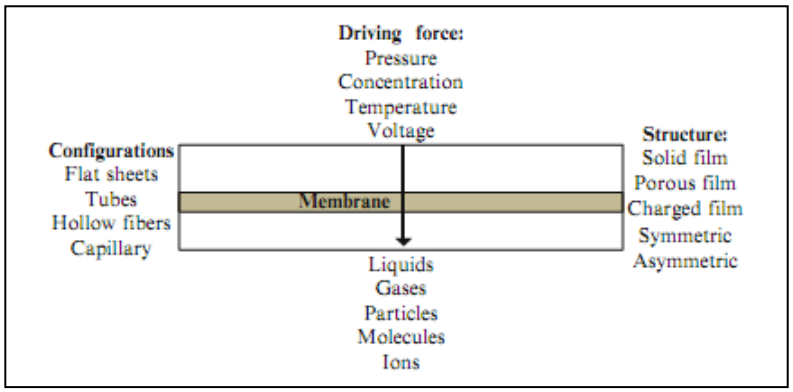


**Fig. 1.2.** Fundamentals of membrane and membrane processes (Wang et al., 2011).

There are many ways to classify synthetic membranes. They can be classified by the nature of the membrane material, the membrane morphology, geometry, preparation methods, separation regime and processes, etc. (Wang et al., 2011).

There are various application of membrane processes on heavy metal removal.

## Reverse osmosis (RO)

Reverse osmosis is a membrane technology widely applied in water desalination, production of potable water and more recently in tertiary wastewater treatment (Pérez-González et al., 2012). It is a process that is inherently simple to design and operate compared with many traditional separation processes such as distillation, extraction, ion exchange, and adsorption. Thus, reverse osmosis is considered as the simplest and most efficient technique for seawater desalination purposes. It is reported that membrane-based desalination accounts for about 44% of the installed capacity of water desalination in the world (Matin et al., 2011).

Hafez et al. (2002) studied on removal efficiency of chromium by using of a pilot-scale setup of 7 and 16 bar RO membrane units at different working pressures and under variable salt concentrations were carried out to remove the hazardous chromium from the spent tanning effluent and recover it for further recycling. The study proved that membrane technique is able to separate chromium efficiently from the pretreated tanning wastewater.

## Ultrafiltration (UF)

Ultrafiltration is a very versatile and widely employed separation process whose nature is between reverse osmosis and microfiltration. Ultrafiltration membranes, with pore sizes typically ranging from $1x10^{-9}$ to $5\times10^{-8}$ m, are capable of retaining species in the molecular weight range of 300-500000 Da (Hamza et al., 1997).

This pressure-driven technique is widely utilized for fractionation, purification, separation and concentration of water soluble solutes or water dispersible materials. Applications can be found in fields such as the chemical industry, metallurgy, paper industry, textile, leather industry, pharmaceutical industry as well as food and dairy industries (Hamza et al., 1997).

Arthanareeswaran et al. (2007) studied on removal of chromium from aqueous solution using cellulose acetate and sulfonated poly (ether ether ketone) blend ultrafiltration membranes. In their study cellulose acetate and sulfonated poly(ether ether ketone) blend ultrafiltration membranes were prepared by precipitation phase inversion technique and subjected to the rejection of chromium at different concentrations with a water-soluble macroligand (polyvinylalcohol).

Aroua et al. (2007) investigated the removal of chromium species from aqueous dilute solutions using polymer-enhanced ultrafiltration (PEUF) process. Three water soluble polymers, namely chitosan, polyethyleneimine (PEI) and pectin were selected for that study.

## Nanofiltration (NF)

It was introduced in the late 1980s, mainly aiming at combined softening and organics removal. Since then, the application range of nanofiltration has

extended tremendously. New possibilities were discovered for drinking water production, providing answers to new challenges such as arsenic removal, removal of pesticides, endocrine disruptors and chemicals, and partial desalination (Bruggen et al., 2008). NF membranes have a high permeability for monovalent salts (e.g., NaCl, KCl), but they are able to eliminate multivalent salts near completely and remove relatively small organic compounds. Also NF was used as an alternative to RO for the concentration and demineralization of whey in dairy industry (Wang et al., 2011).

Hafiane et al. (2000) studied on removal of hexavalent chromium by nanofiltration. They reported that NF is a very promising method of treatment for waste water charged with hexavalent chromium.

Ren et al. (2010) investigated the feasibility of employing nanofiltration for the removal of Cr(VI) from wastewater. They used poly(m-phenyleneisophthalamide) (PMIA) to fabricate asymmetric nanofiltration membrane through the phase-inversion technique. Separation experiments for Cr(VI) salt solution indicate that PMIA NF membranes can be effectively employed in the treatment of Cr(VI) contaminated water under alkaline condition based on the interaction between the negatively charged membrane and Cr(VI) ions.

**Microfiltration**

Microfiltration membranes are used for separation of impurities (particles, viruses, and bacteria) with a size range of 0.1–10 μm from solvent or other low molecular weight components. The separation mechanism is based on a sieving effect and particles are separated according to their dimensions although some charge or adsorptive separation is possible. The applied pressure in MF is quite low (<2 bars) compared with other filtration processes (Wang et al., 2011).

Danış (2005) examined removal of chromate ions from water by red mud that is an adsorbent, using cross flow microfiltration. Under certain conditions, (pH = 5.2) the chromate rejection reached a maximum of 100% rejection. It was observed that the efficiency of the chromate removal increased with increasing red mud/chromate concentration ratio; however, the steady-state permeate flux decreased with an increasing red mud/chromate ratio. Also the rejection of chromate decreased with increasing membrane pore size. On the contrary,

permeate flux increased with increasing membrane pore size. The method was found to be effective in removing chromate from water.

Vasanth et al. (2012) investigated the preparation of ceramic microfiltration membrane from inexpensive raw materials such as kaolin, quartz, calcium carbonate by uniaxial dry compaction method. The separation performance of the membrane in terms of flux and removal of chromium(VI) ion using baker's yeast biomass as a function of applied pressure, pH, metal ion concentration and biomass dosage was also studied. At lower pH, the metal solution shows higher removal. They also observed that the removal of Cr(VI) ion increases with increasing the biomass concentration and decreases with increasing the metal ion concentration. The removal of Cr(VI) was found to be independent of the applied pressure.

## Electrodialysis

Electrodialysis can be considered as a conventional technique for metals removal (Prados and Gutiérrez-Cervelló, 2011). The removal of ionic components from aqueous solution through ion exchange membranes is carried out under the driving force of an electrical field. When a direct current potential is applied between two electrodes, the positively charged cations move to the cathode, passing through the negatively charged cation exchange membrane and retained by the positively charged anion exchange membrane. While the negatively charged anions move to the anode, passing through the anion exchange membrane and retained by the cation exchange membrane. At the end ion concentrations increase in alternate compartments with a simultaneous decrease of ions in other compartments (Kabay et al., 2008).

Nataraj et al. (2007) investigated the removal of chromium ions in its hexavalent oxidation state using electrodialysis (ED) pilot plant comprising a set of ion-exchange membranes. Significant results were obtained with lower initial concentrations of less than 10 mg/L. In this research they reported the ED plant was found to be appropriate to produce good quality drinking water from the simulated mixture by removing the unwanted ions.

Lambert et al. (2006) examined on treatment of solutions containing trivalent chromium by electrodialysis. In this study, a two-step Cr(III) separation–concentration process is proposed. In the first step, a cation-exchange membrane,

Nafion®117, modified by electrodeposition of polyethylenimine (PEI) was used to separate successfully Cr(III) from NaCl solutions. In the second step, conventional electrodialysis with Nafion® 117, Nafion® 324 or CMX membranes permits to increase the concentration of Cr(III) in the solutions produced in the separation stage. They reported that in this study pH control in the dilute compartment is crucial. The pH may be adjust to increase the current efficiency of the both chromium and sodium ion and avoid the chromium precipitation.

## 1.2. Solvent Impregnated Resins (SIRs)

Traditional technologies used for metal separation and recovery are being substituted by emerging technologies such as membrane separation, electrodialysis and selective adsorption. In the last case, a great effort has been made towards the synthesis of new metal complexing extractants, ion-exchangers and polymeric adsorbents capable of improving the efficiency and selectivity for a wide range of metal species (Cortina et al., 1998). Systems of this type combine characteristics of ion exchange with liquid–liquid extraction and have led to the development of solvent impregnated resins (SIR) (Saha et al., 2004). Warshawsky and Grinstead were the first to describe the synthesis and applications of solvent impregnated resins (SIRs) in 1971 (Trochimczuk et al., 2004).

Solvent impregnated resins (SIRs) can be considered as alternative adsorbent materials since they are similarly capable of selective sorption. SIRs comprise a polymeric matrix impregnated with readily available liquid ionic extractants, are relatively easy to prepare and they combine the unique features and process advantages of liquid–liquid extraction and ion exchange (Kabay et al., 2010). The concept provides a possibility to obtain a diversity of chelating sorbents using simple inexpensive impregnation techniques. In other words, the ease of preparation method allows exploiting a wide spectrum of highly selective extractants supplying their functionality to suitable polymeric matrixes (Zagorodni, 2007). Thereafter, SIRs containing various liquid ionic extractants, e.g. amines (such as Kelex 100 – 7-(4-ethyl-1-methyloctyl)-8-quinolinol), phosphoric, phosphinic, thiophosphinic acids and esters (for example 2-ethylhexyl phosphoric acid and bis ([2,4,4-trimethylpentyl] monothiophosphinic acid) or solvating extractants (tributyl phosphate, trioctyl phosphine oxide, octyl(phenyl)-N,N-diisobutyl-carbamoylmethylphosphine oxide and more recently dimethyl dibutyl tetradecyl-1,3-malonamide) have been synthesized and investigated for a range of potential applications (Trochimczuk et al., 2004).

The model of the impregnated resin can be envisaged as a liquid complexing agent dispersed homogeneously in a solid polymeric medium. The impregnating extractant behaves as in the liquid state, while exhibiting strong affinity to the matrix. For the ‘‘ideal’’ SIR, the properties of which are characterised as:

- good mobility of the extractant inside the material phase and good mobility of exchangeable counterion (a complexing metal ion in most of the applications) between aqueous and exchanger phases,
- high ion selectivity,
- high binding capacities,
- good chemical and physical stability and low losses of the extractant. (Zagorodni, 2007, Saha et al., 2004).

The impregnating reagent can interact with the surrounding solution without losing contact with the support. Hence, impregnated resins can be considered as chelating resins whose functional groups are not chemically bounded to the matrix but physically adsorbed on it (Zagorodni, 2007). As it is seen from Figure 1.3, the organic extractant E is contained inside the pores of a porous particle. On the one hand the solute S, which is initially dissolved in the aqueous phase, dissolves in the organic extractant phase during the extraction process. On the other hand, it can react with the extractant to form a complex ES. Complexation of the solute with the extractant shifts the extraction equilibrium further towards the organic phase. This way, the solute extraction is enhanced (Burghoff et al., 2008).

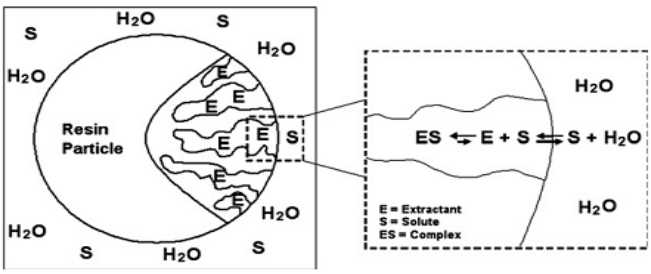


**Figure 1.3.** Schematical illustration of a SIR particle and the extraction mechanism (Burghoff et al., 2008).

The comparison of solvent extraction with ion exchange is presented in Table 1.1. As one can see, the impregnated materials are intermediate between solvent extraction and ion exchange. The only common drawback is a low capacity in comparison with both conventional techniques. As a result, the use of

impregnated materials is more advantageous in analytical separations, particularly in analytical chromatography. The analytical applications also allow use of the material in moderate number of cyclic operations. Nevertheless, certain advantages of the impregnated materials can also be foreseen for preparative and industrial separations (Zagorodni, 2007).

**Table 1.1.** Separation with solvent impregnated resins in comparison with two other techniques (Zagorodni, 2007).

| Comparison with solvent extraction | Comparison with ion exchange |
|---|---|
| **Advantages** | |
| • Possibility to design column processes<br>• Possibility to treat very dilute solutions<br>• High contact surface area without any mixing<br>• Less reagent loss at cyclic operations | • Extremely high variety of extractants which can be incorporated into the polymer beads<br>• Lower cost of preparation<br>• Faster mass transfer in many cases |
| **Disadvantages** | |
| • Less percentage of the reagent use and less capacity<br>• Higher cost | • Low capacity<br>• Instability at cyclic operations |

The only limitation of solvent impregnated resins in industrial applications is the loss of extractant from the polymer matrix since there is no covalent attachment of extractant to the polymer network (Kabay et al., 2004b). Leakage of the extractant from the polymeric support leads to a steady loss of sorptive capacity towards targeted ions thereby rendering SIRs ineffective after several cycles of application. Moreover, this leakage is not acceptable from an environmental point of view as the leachate is likely to contain toxic and odorous compounds (amines, thiophosphinic acids and esters, etc.) that will contaminate effluents (Kabay et al., 2005). It is surprising that so little effort has been devoted to research aimed at increasing the stability of the SIRs (Trochimczuk et al., 2004).

### 1.2.1 Preparation of SIRs

Solvent impregnated resins are simply prepared by immobilization of a complexing solvent extraction reagent within the matrix structure of polymer

adsorbents by physical contact (Kabay et al., 2004b). The following requirements are essential for the preparation of an efficient impregnated resin;

- the extractant must be a liquid or retained in the liquid state by addition of a diluents (usually an organic solvent);
- both the extractant and the diluent should have minimal solubility in the aqueous solutions which are supposed to be treated with the obtained material;
- the polymeric support should be fully expanded during the impregnation process and remain so. Hence, macroporous supports that show minimum volume variations are preferred;
- the impregnation method should not affect properties of the extractant or the supporting polymer (Saha et al., 2004; Zagorodni, 2007).

Several impregnation methods with a number of variations have been proposed. The two most conventional roots, so called dry and wet impregnations, are illustrated in Fig. 1.4. Dry method is most successful in the impregnation of hydrophilic extractants such as amines, ethers, ketones, etc (Zagorodni, 2007).

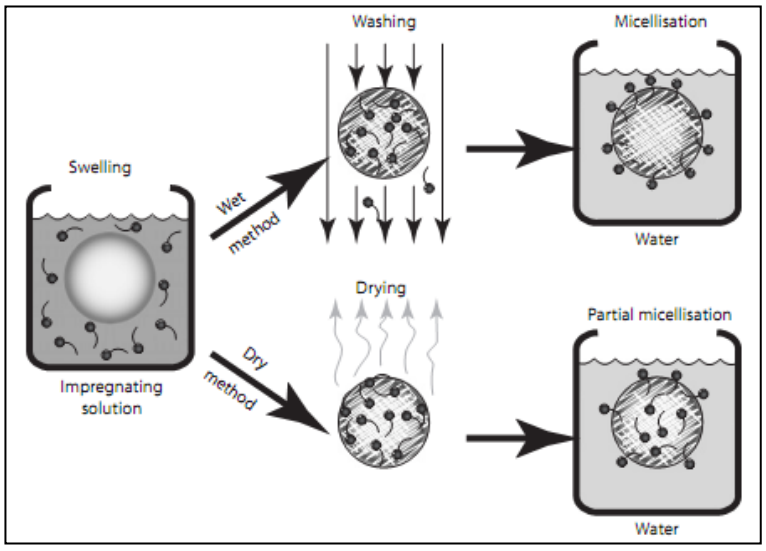


**Fig. 1.4.** Two most conventional methods for preparation of solvent impregnated resins: wet (upper branch) and dry (bottom branch) (Zagorodni, 2007).

Another approach is the modifier addition method. The modifier, such as, dibutylpolypropylene glycol, is there to promote water penetration into the polymer. Different impregnation methods result in different composition of obtained materials (Zagorodni, 2007) that is illustrated in Table 1.2.

**Table 1.2.** Composition of impregnated materials obtained with different impregnating methods (Zagorodni, 2007).

| **Impregnation method** | **Composition** |
|---|---|
| Dry impregnation | Polymer – extractant |
| Wet impregnation | Polymer – extractant – organic solvent |
| Modifier addition followed by drying | Polymer – extractant – modifier |
| Modifier addition followed by washing | Polymer – extractant – modifier – organic solvent |

Peculiar properties of a particular material depend on the type of the extractant and also on the selected impregnation method. (Zagorodni, 2007).

So far as weak, usually van der Waals, forces are responsible for the binding of the extractant, the most important feature of the support is its surface. The physical structure can be both gel-type and macroporous but, macroporous is used more commonly (Zagorodni, 2007). Normally, non functionalized polymer beads are impregnated with metal extraction reagents, at the same time the matrix can be functionalized (Zagorodni, 2007; Cortina et al., 1998).

Saha et al. (2004) prepared SIR using Amberlite XAD-7 resin as non-functionalized support and Aliquat 336 as an extractant by a wet impregnation technique. They used the SIRs for removal of Cr(VI).

Another example of SIR preparation is investigation of Matsunaga et al. (2001). They used Amberlite XAD-2, XAD-4, XAD-16 and XAD-7 resins as a polymeric support and 2-ethylhexyl hydrogen 2-ethylhexyl phosphonate (PC-88A) as an extractant. They synthesized SIRs by dry method. The products were dried in vacuo at 50°C. They used the SIRs for extraction of rare earth elements such as La(III), Sm(III), Tb(III) and Yb(III).

One more type of selective ion exchange resins are Levextrel resins. The Levextrel resins are sorbents similar to the solvent impregnated resins. They differ in the preparation method. Levextrel resins are obtained by the introduction of extractants in the mixture of monomer(s) prior to the synthesis of the material. (Zagorodni, 2007).

### 1.2.2 Stabilization of SIRs

The main disadvantage of SIRs is the loss of extractant due to solubility in the aqueous phase. Leakage of the extractant from the polymeric support leads to a steady loss of sorptive capacity towards targeted ions thereby rendering SIRs ineffective after several cycles of application (Trochimczuk et al., 2004). Several methods have been studied to overcome the problems associated with operational stability and to try and stabilize SIRs. They can be divided into two groups:

- Removal of part of the extractant that is loosely attached to the support.
- Post-impregnation formation of a protective barrier around beads of SIR (Kabay et al., 2010).

Generally, the methods of the first group are aimed at the removal of any extractant that has not interacted with the surface of the polymeric support. The extractant removal is done by carrying out several metal extraction cycles and is essentially an accelerated form of leaching. Alternatively, freshly prepared SIR can be kept for several hours in hot water. This has a similar effect on the stability of the resin since the solubility of the extractant in water is positively affected by the temperature. An alternative way of increasing the stability of SIRs is to improve the polymeric support-extractant system so that interactions are maximized and the solubility of the extractant in water is minimized (Kabay et al., 2010).

The post-impregnation encapsulation is the most promising but most complicated stabilization technique. It is based on the idea that the loss of the extractant can be prevented by supplying a semipermeable coat around each bead of the material. The coating must allow rapid diffusion of target ions but retain the organic extractant and the extractant-ion complexes (Zagorodni, 2007).

Trochimczuk et al. (2004) studied stabilization of SIRs. In that study Aliquat 336 impregnated resins (SIRs) have been stabilized by the formation of a surface coating consisting of crosslinked poly(vinyl alcohol). Kabay et al. (2004b), worked on column mode Cr(VI) removal with stabilized SIRs. The results showed that with coated SIRs only a small decrease was observed after four cycles with column study. The schematic idea of the modification is presented in Figure 1.5.

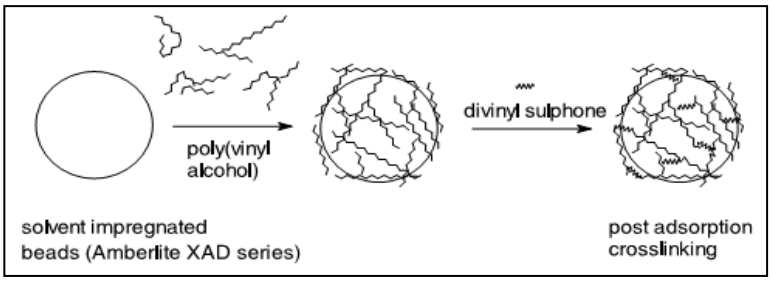


**Figure 1.5.** Scheme of the preparation of coated solvent impregnated resins (Trochimczuk et al., 2004).

Kabay et al. (2005) studied on Cr(VI) removal with stabilized Aliquat 336 impregnated Amberlite XAD-4. There was a significant decrease in breakthrough capacity of uncoated SIR due to a gradual leakage of extractant. The loss of Aliquat 336 from coated SIR was small over five sorption/elution cycles.

### 1.2.3 Utilization of SIRs for removal of heavy metals

Solvent impregnated resins (SIR) have been used in various applications for the treatment of metal effluents containing heavy metals (Kabay et al., 2003). In the literature there are many papers that mention about utilization of SIRs for removal of heavy metals.

Kabay et al. (1998) reported on extraction of Cd(II) and Cu(II) from 40% $H_3PO_4$ solution by using Amberlite XAD-2, XAD-4, XAD-7 and XAD-8 as polymeric support containing Cyanex 302 (bis [2,4,4-trimethylpentyl] monothiophosphinic acid).

Serarols et al. (2001) run the adsorption of Au(III) and Zn(II) by impregnated resins in batch and column experiments. They used triisobutyl phosphine sulphide (TIBPS) (Cyanex 471) and di(2-ethylhexyl) phosphoric acid (DEHPA) impregnated Amberlite XAD-2 resins for this purpose respectively.

Kabay et al. (2004b) studied on Cr(VI) removal using Aliquat 336 impregnated Amberlite XAD-4 that was stabilized by the formation of a surface coating consisting of cross-linked poly(vinyl alcohol). The effect of coating and the degree of crosslinking on chemical stability of SIRs were studied by running four sorption–washing–elution–washing cycles. The chemical stability of impregnated resins was monitored after each cycle by nitrogen analysis. The decrease in nitrogen content of uncoated resins was significant after each cycle. In the case of coated SIRs, only a small decrease was observed after one cycle.

Saha et al. (2004) investigated the removal of chromium (VI) from aqueous solution using Aliquat 336 impregnated Amberlite XAD-7. They found that the sorption of Cr(VI) was most effective at pH 6. Cr(VI) sorption capacity of the SIR increases with increasing impregnation ratio. Kinetic studies confirmed that more than 50% of Cr(VI) removal took place within the first 7 min for all SIR.

Yuan et al. (2010) studied on In(III) adsorption with coated solvent impregnated resins. They prepared coated solvent impregnated resins by the formation of PVA–boric acid protective layer on solvent impregnated resins (SIRs) containing 2-ethylhexyl phosphoric acid mono (2-ethylhexyl) ester (EHEHPA).

Hosseini-Bandegharaei et al. (2011) studied on Hg(II) adsorbent. The SIR was prepared by impregnating 1-(2-thiazolylazo)-2-naphtol (TAN) onto Amberlite XAD-4 resin beads. It was reported that the new SIR could be successfully recycled for several consecutive cycles without significant loss in its sorption capacity.

Another application of impregnation technique was reported by Vellaichamy and Palanivelu (2011). They synthesized di-(2-ethyl hexyl phosphoric acid) (D2EHPA) and tri-n-octyl phosphine oxide (TOPO) mixture impregnated multiwalled carbon nano tubes (MWCNTs) for preconcentration and separation of copper, nickel and zinc in aqueous samples.

## 1.3 Aim of the study

In this study, removal of Cr(VI) ions by solvent impregnated resins prepared using various polymeric adsorbents was studied. Comparison of Cr(VI) removal performances of Aliquat 336 impregnated Diaion HP 20 and Diaion HP 2MG was done. Besides P(ClVBTA) and P(ClAPTA) ion exchange resins were synthesized in University of Concepcion in order to perform of Cr(VI) removal. Also ability of these resins for C(VI) removal was compared with that of commercial resin Amberlite IRA-400.

# 2. EXPERIMENTAL

## 2.1 Materials

### 2.1.1 Polymeric adsorbents

Hydrophobic styrene–divinylbenzene based Diaion HP 20 and hydrophilic methacrylic based Diaion HP 2MG that were provided by Mitsubishi Chem. (Japan) were used as polymeric adsorbent (Figure 2.1). The properties of polymeric adsorbents are given in Table 2.1.

a) b)

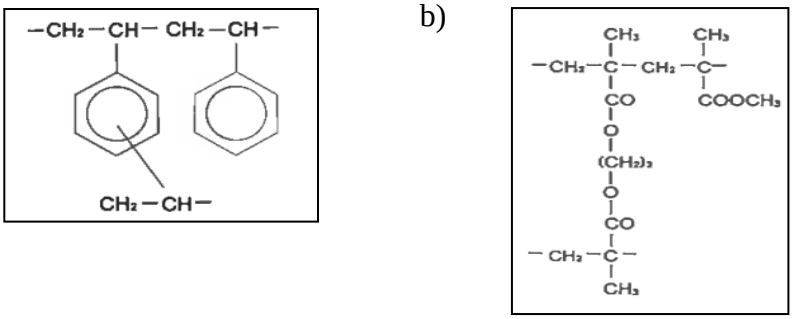

**Figure 2.1** Structure of polymeric adsorbents **a)** Diaion HP 20 **b)** Diaion HP 2MG.

**Table 2.1** Properties of polymeric adsorbents.

| **Polymeric adsorbent** | Diaion HP 20 | Diaion HP 2MG |
|---|---|---|
| **Matrix** | Styrene–divinylbenzene | Methacrylic |
| **Physical form** | White beads | White beads |
| **Moisture content (%)** | 56.50 | 61.10 |
| **Swelling (mL/g)** | 3.45 | 3.67 |
| **BET surface area ($m^2$/g)** | 524.16 | 556.81 |
| **Pore volume (mL/g)** | 1.18 | 1.15 |
| **Particle size (mm)** | 0.50-0.71 | 0.50-0.71 |
| **Specific gravity (g/mL)** | 1.01 | 1.09 |

### 2.1.2 Ion exchange resins

Amberlite IRA-400 that has quaternary ammonium groups. The properties of Amberlite IRA-400 were given in Table 2.2. Structures of Amberlite IRA-400 and synthesized resins in Concepcion University P(ClVBTA) and P(ClAPTA) were given in Figure 2.2.

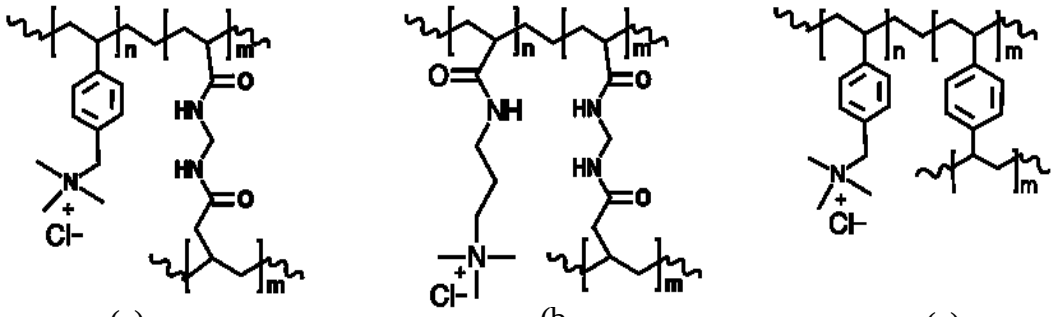


**Figure 2.2** Structure of ion exchange resins **a)** P(ClVBTA) **b)** P(ClAPTA) **c)** Amberlite IRA-400.

**Table 2.2** Properties of Amberlite IRA-400.

| | |
|---|---|
| **Matrix** | styrene/divinylbenzene (gel type) |
| **Moisture content (%)** | 40-47 |
| **Particle size (mm)** | 0.60-0.75 |
| **Cross-linkage (%)** | 8 |
| **Matrix active group** | quaternary ammonium functional group |
| **Limit temperature (°C)** | 60 |
| **Operating pH** | 0 - 14 |
| **Capacity (meq/mL by wetted bed volume)** | 1.4 |

## 2.1.3 Chemicals

Quaternary ammonium salt Aliquat 336 (trioctylmethylammonium chloride) (Sigma Aldrich), acetone (Merck, 99.8 %) were used in impregnation procedure. For extractant Aliquat 336 is well known commercial solvent extraction reagent consists of a mixture of the chloride salts of a number of long alkyl chain quaternary ammonium ions.

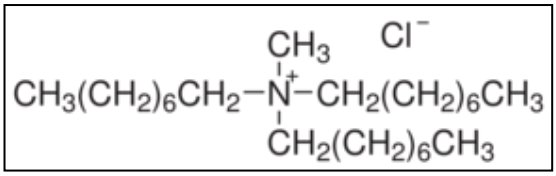

**Figure 2.3** Proposed molecular structure of Aliquat 336 extractant.

$K_2CrO_4$ (Merck) and HCl (Merck, 30%) were used in to prepare of Cr(VI) solution at pH 4.

NaOH (J. T. Beaker, 97%) and NaCl (Riedel, 99.8%) were used to prepare elution solution for column study.

To synthesize ion exchange resins, (4-vinylbenzyl) trimethylammonium chloride (99%, Aldrich) and (3-acrylamidopropyl) trimethyl ammonium chloride (75 wt. % solution in water, Aldrich) were used as monomers in the polymerization step, *N*,*N*-methylene-*bis*-acrylamide (99%, Aldrich) and ammonium peroxidisulfate (98%, Aldrich) were used as cross-linker and initiator respectively.

## 2.2 Equipments

### 2.2.1 Equipments used in impregnation procedure

- **Shaker:** Selecta – Unitronic OR shaker (Figure 2.4)

**Figure 2.4** Selecta – Unitronic OR shaker

- **Filtration equipment:** PALL Corporation Filtration Assembly and GAST Laboratory Oilless Diaphragm Vacuum Pump & Compressor (Figure 2.5)

**Figure 2.5** Filtration apparatus used for filtration and washing adsorbents (PALL Vacuum Pump filtration flask & funnel)

- **Vacuum oven:** Gallen Kamp (Figure 2.6)


**Figure 2.6** Gallen Kamp vacuum oven.

### 2.2.2 Equipments used in batch-mode sorption studies

- **Balance:** Precisa XB 220A
- **Shaker:** Selecta-Unitronic OR shaker (Figure 2.4)**Water bath and Mechanical stirrer:** Nüve BM 302 water bath, Velp Scientifica Stirrer DLH (Figure 2.7)


**Figure 2.7** Nüve BM 302 water bath, Velp Scientifica Stirrer DLH

- **Syringe:** SET İnject
- **Filter:** Millipore Millex-FH 0.45 µm filter

### 2.2.3 Equipments used in column sorption-elution studies

- **Glass column:** ID=0.7cm
- **Peristaltic pump:** Ismatec ISM 834
- **Fraction collector:** Advantec CHF100SA

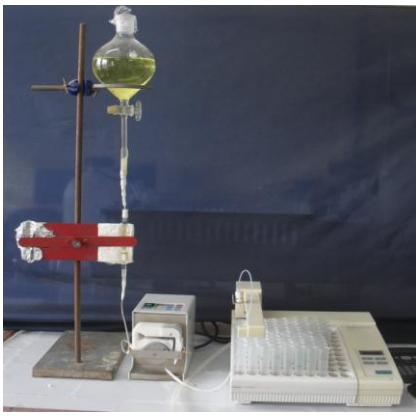

**Figure 2.8** Column system

### 2.2.4 Equipments used in synthesis of ion exchange resins

- **Polymerization reactor:** Schlenk polymerization tube
- **Heater:** IKA C-MAG HS 7 (Figure 2.9)
- **Oven:** Equilab Memmert

**Figure 2.9** Polymerization system

### 2.2.5 Equipments used in characterization of ion exchange resins

- **Fourier transformed infrared spectroscopy (FTIR):** Perkin Elmer 1760-X spectrometer.

### 2.2.6 Analysis of chromium

- **Atomic absorption spectrophotometers:** VARIAN Spectra AA atomic absorption spectrophotometer (Figure 2.10) used at Ege University and Unicam Solar model atomic absorption spectrometer (AAS) used at University of Concepcion.

**Figure 2.10.** VARIAN Spectra AA atomic absorption spectrophotometer

## 2.3 Methods

### 2.3.1 Impregnation procedure for solvent impregnated resins (SIRs)

Polymeric adsorbents Diaion HP 20 and Diaion HP 2MG were immersed into Aliquat 336 solution in acetone separately. SIRs were prepared in the ratio of 1 g-Aliquat 336/g-resin, 2 g-Aliquat 336/g-resin and 3 g-Aliquat 336/g-resin in 5 mL acetone. The mixtures were shaken at 25°C for 24 h in water bath. After that SIRs were separated by filtration using a sintered glass funnel and washed with deionized water. The resins were air dried firstly after dried under vacuum at 40°C.

### 2.3.2 Batch sorption tests with SIRs

#### 2.3.2.1 Determination of optimum SIR amount

In this study, the various amounts (0.010, 0.025, 0.050, 0.100, 0.150, 0.200 g) of SIRs were contacted with 50 mL of 20 mg/L Cr(VI) solution at pH 4.0. In this thesis pH 4.0 was taken as optimum according to study of Kabay et al (2003). The experiment was performed at 25°C, 70 rpm shaking rate for 24 h using a shaker.

#### 2.3.2.2 Kinetic studies with SIRs

Kinetic studies were performed using 0.75 g Aliquat 336 impregnated HP 20 in the ratio of 1 g-Aliquat 336/g-resin, 1.5 g Aliquat 336 impregnated HP 20 in the ratio of 2 g-Aliquat 336/g-resin, 0.75 g solvent impregnated HP 20 in the ratio of 3 g-Aliquat 336/g-resin, 0.75 g solvent impregnated HP 2MG in the ratio of 1 g-Aliquat 336/g-resin, 1.5 g solvent impregnated HP 2MG in the ratio of 2 g-Aliquat 336/g-resin and 0.75 g solvent impregnated HP 2MG in the ratio of 3 g-Aliquat 336/g-resin according to results of optimum resin amounts using these

SIRs. The SIRs were immersed into 750 mL of 20 mg/L Cr(VI) solution at pH 4 separately and stirred at 250 rpm at 25°C using mechanical stirrer. At different times (5, 10, 15, 20, 30, 45, 60, 120, 180, 240, 360, 480 and 1440 min) 4 mL samples were taken by injector and filtered by membrane filter with 0.2 μm of pore size.

### 2.3.3 Column sorption-elution tests with SIRs

A series of column-mode sorption/elution studies for removal of Cr(VI) from aqueous solution at pH 4 have been carried out with Aliquat 336 impregnated Diaion HP 20 and Diaion HP 2MG. A 0.5 mL of wet SIRs were packed into a glass column that has 0.7 mm of internal diameter. To fix the resin bed, a glasswool was used above the resin. A 20 mg/L of Cr(VI) solution at pH 4 was passed downflow through the column using a peristaltic pump at a space velocity (SV) of 15 $h^{-1}$. Effluents were collected continuously by fraction collector as 5 mL successively. The elution of chromium from the loaded resin was carried out using a solution of 1M NaOH–1M NaCl mixture at a SV of 5 $h^{-1}$. The column elution profiles were obtained by analysis of each successive 3 mL fractions of eluats.

### 2.3.4 Synthesis of ion exchange resins

The ion exchange resins poly[(Ar-vinylbenzyl)trimethylammonium chloride] P(ClVBTA) and poly[(3-Acrylamidopropyl) trimethyl ammonium chloride] P(ClAPTA) were prepared by free-radical polymerization. The synthesis of P(ClVBTA) was run in a polymerization flask. For this purpose (4-vinylbenzyl) trimethylammonium chloride and 8 mol % *N*,*N*-methylene-*bis*-acrylamide as cross-linker were mixed with approximately 50 mL of water and stirred on a magnetic stirrer. After that, 1 mol % ammonium peroxidisulfate as initiator was added and kept under $N_2$ at 70°C for 24 h. Then, the resin was filtered and washed with distilled water and dried up to constant weight at 50°C. Synthesis of P(ClAPTA) was performed in the same way.

### 2.3.5 Material characterization

The characterizations of polymers P(ClVBTA) and P(ClAPTA) were carried out by Fourier transformed infrared spectroscopy (FTIR) on a Perkin Elmer 1760-X spectrometer from 4000 to 400 $cm^{-1}$ using KBr pellets.

### 2.3.6 Batch sorptions with ion exchange resins

#### 2.3.6.1 Effect of pH on the sorption of Cr(VI)

To investigate the effect of pH on aqueous solutions for P(ClVBTA) and P(ClAPTA), 30 mg resin was contacted 5 mL of 30 mg/L Cr(VI) solutions at different pHs (2, 4, 6 , 8, 10, 12). The experiment was performed at 25°C, 140 rpm shaking rate for 24 h. After 24 h, samples were put out and filtered into a volumetric flask. Resins were washed with distilled water and diluted to 50 mL. Cr(VI) concentrations before and after sorption were analyzed by Unicam Solar model atomic absorption spectrometer (AAS).

#### 2.3.6.2 Equilibrium studies

The sorption isotherms of Cr(VI) ions were obtained using the batch technique at the optimum pH. For this purpose, 30 mg of resins were contacted with 5 mL Cr(VI) solution at the optimum pH 9. The study performed at 25, 35 and 45°C, 140 rpm for 24 h and various concentration of Cr(VI) (100, 200, 300, 400, 500, 600, 700 mg/L). Cr(VI) concentrations before and after sorption were analyzed by AAS.

#### 2.3.6.3 Kinetic studies

Kinetic studies were performed with different test tubes containing P(ClVBTA) and P(ClAPTA). 30 mg resin was contacted with 5 mL 30 mg/L Cr(VI) solution at pH 9 by shaking with shaker in 140 rpm at 25°C. Samples were put out at different contact time (1, 3, 5, 7, 10, 15, 20, 30, 60, 120, 240, 360, 600, 720, 1140 min). Cr(VI) concentrations were monitored by AAS.

#### 2.3.6.4 Selectivity studies

In this study, 30 mg P(ClVBTA) and P(ClAPTA) were immersed into 5 mL of 30 mg/L Cr(VI) solution that contains 500 mg/L of $Cl^-$ and 500 mg/L of $SO_4^{2-}$ separately at pH 9. Solution and resins were contacted in a shaker at 25°C and 140 rpm for 24 h. The samples were analyzed by AAS.

# 3. RESULTS AND DISCUSSION

## 3.1 Batch-mode Sorption of Cr(VI) by SIRs

### 3.1.1 Determination of optimum amount of SIR

The optimum resin amounts for Cr(VI) removal were determined using HP 20 and HP 2MG based SIRs prepared at impregnation ratios of 1 g Aliquat 336/g-resin, 2 g Aliquat 336/g-resin and 3 g Aliquat 336/g-resin. As shown in Figure 3.1, for HP 20 based SIRs, the optimum SIR amounts were found as 0.1000 g for all impregnation ratios. Also with HP 2MG based SIRs, it was found that 0.1000 g was optimum amount of resin for all impregnation ratios as is seen from Figure 3.2. For HP 20 based SIR Cr(VI) removal were 97%, 88%, 92%, for the impregnation ratios of 1 g Aliquat 336/g-resin, 2 g Aliquat 336/g-resin, 3 g Aliquat 336/g-resin, respectively. For HP 2MG based SIRs, Cr(VI) removal were 98%, 91%, 93%, for the impregnation ratios of 1 g Aliquat 336/g-resin, 2 g Aliquat 336/g-resin, 3 g Aliquat 336/g-resin, respectively.

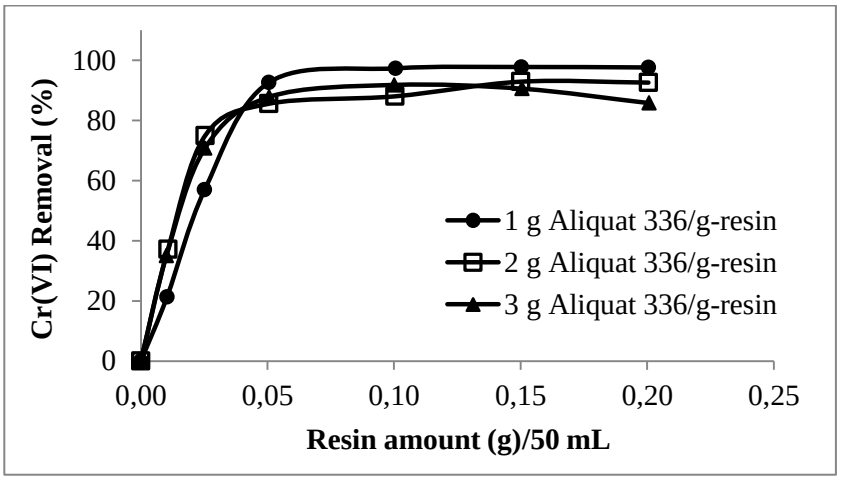


**Figure 3.1.** Effect of impregnation ratio on Cr(VI) removal using HP 20 based SIRs.

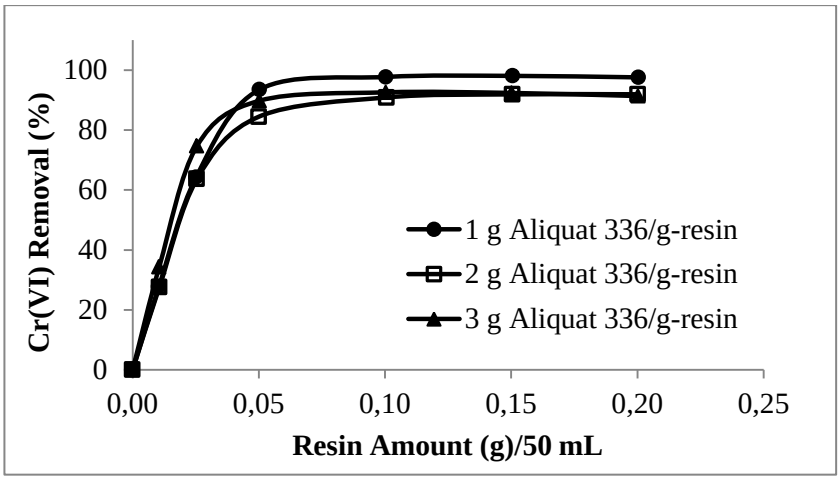


**Figure 3.2.** Effect of impregnation ratio on Cr(VI) removal using HP 2MG based SIRs.

### 3.1.2 Adsorption Isotherms

Equilibrium sorption isotherms are one of the most important studies to design adsorption processes. Moreover, isotherms provide useful information on the interaction between the adsorbate and the adsorbent (Urbano et al., 2012). Equilibrium data were obtained for Cr(VI) sorption onto HP 20 and HP 2MG based SIRs. Adsorption isotherms were obtained using data of optimum resin amount of SIRs. For this purpose, the sorption data were evaluated using Langmuir (Eq. 3.1) and Freundlich (Eq. 3.2) adsorption isotherm models.

The Langmuir isotherm;

$$\frac{C_e}{Q_e} = \frac{1}{Q_{max} b} + \frac{C_e}{Q_{max}} \qquad (3.1)$$

The Freundlich isotherm;

$$\log(q_e) = \log(k_F) + \frac{1}{n}\log(C_e) \qquad (3.2)$$

where $C_e$ is the equilibrium concentration (mg/L), $Q_e$ is the amount of Cr(VI) sorbed at equilibrium (mg/g), and $Q_{max}$ and b are the Langmuir constants related to sorption capacity and energy of sorption, respectively (Hosseini-Bandegharaei et al., 2010). $k_F$ is the Freundlich constant and is related to the sorption efficiency, and n is a dimensionless variable indicative of favourability of sorption (Urbano et al., 2012).

The linearized plots of Langmuir and Freundlich isotherms are given in Figures 3.3–3.14. The experimental data for HP 20 and HP 2MG based SIRs at the impregnation ratio of 1g Aliquat 336 / g-resin fits well to Langmuir model whereas the adsorption data of SIRs with the impregnation ratios of 2g Aliquat 336 / g-resin and 3g Aliquat 336 / g-resin fit well to Freundlich model.

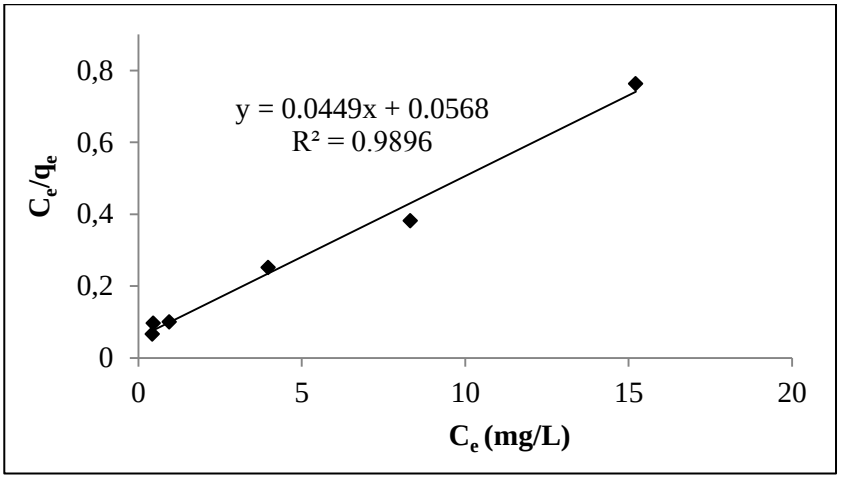


**Figure 3.3.** Linearized form of Langmuir isotherm for HP 20 based SIR at the impregnation ratio of 1 g Aliquat 336 / g-resin.

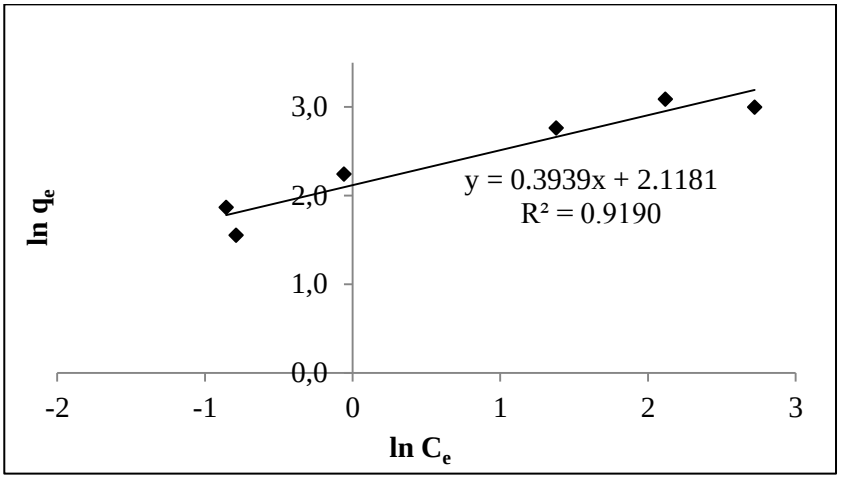


**Figure 3.4.** Linearized form of Freundlich isotherm for HP 20 based SIR at the impregnation ratio of 1 g Aliquat 336 / g-resin.

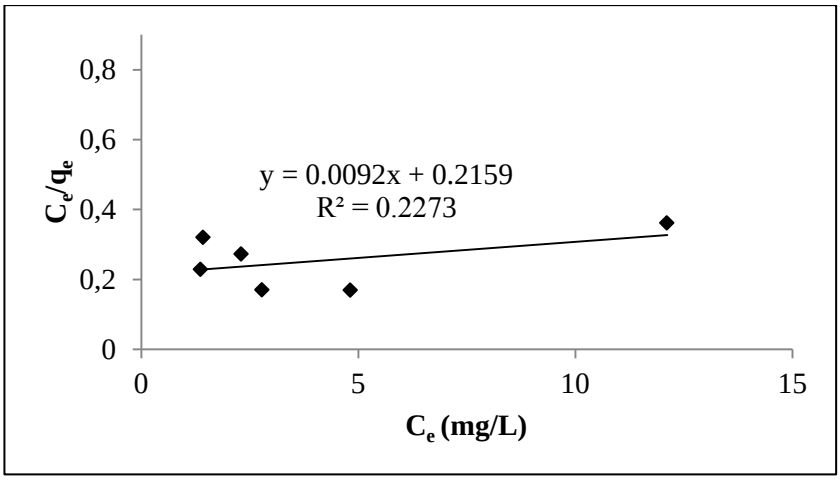


**Figure 3.5.** Linearized form of Langmuir isotherm for HP 20 based SIR at the impregnation ratio of 2 g Aliquat 336 / g-resin.

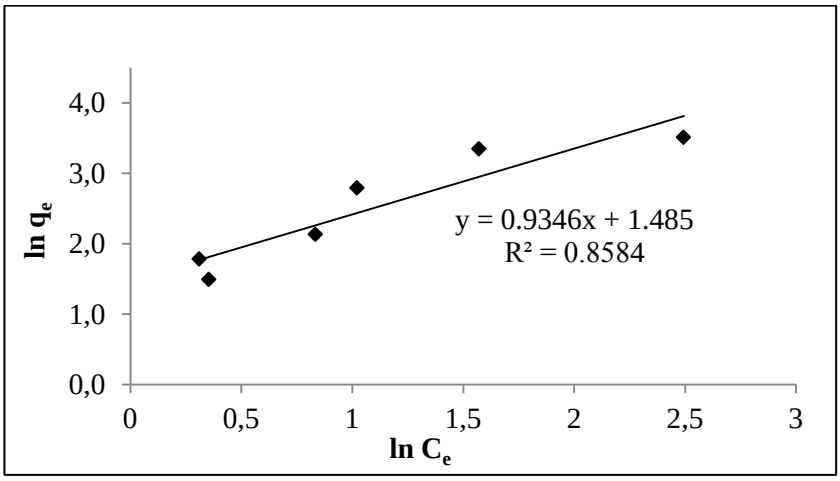


**Figure 3.6.** Linearized form of Freundlich isotherm for HP 20 based SIR at the impregnation ratio of 2 g Aliquat 336 / g-resin.

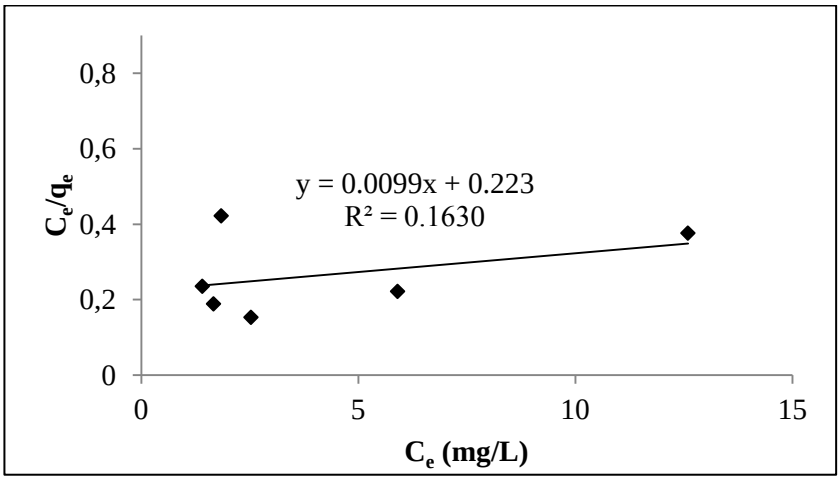


**Figure 3.7.** Linearized form of Langmuir isotherm for HP 20 based SIR at the impregnation ratio of 3 g Aliquat 336 / g-resin.

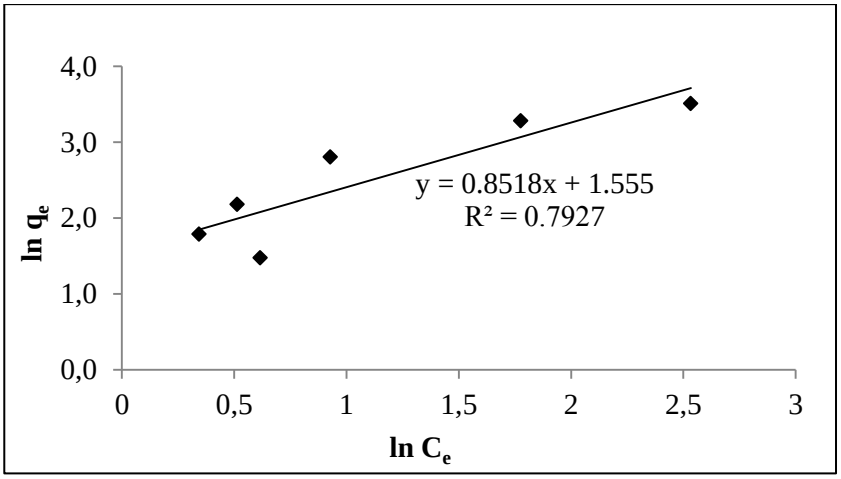


**Figure 3.8.** Linearized form of Freundlich isotherm for HP 20 based SIR at the impregnation ratio of 3 g Aliquat 336 / g-resin.

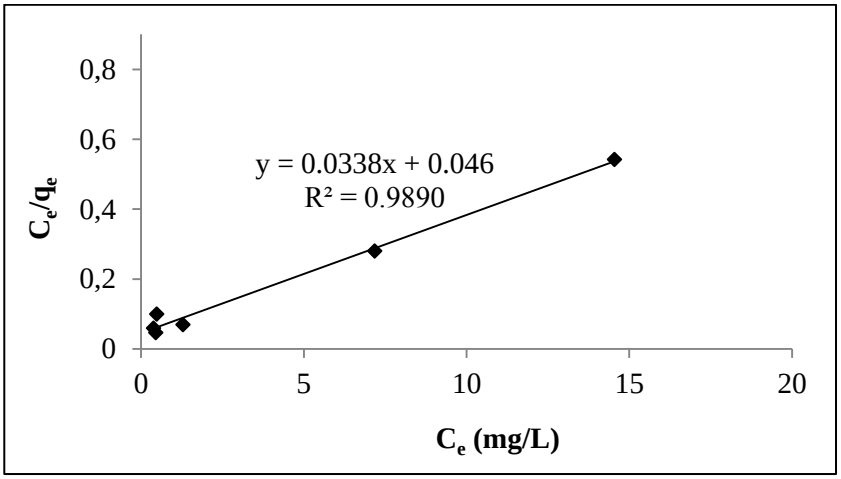


**Figure 3.9.** Linearized form of Langmuir isotherm for HP 2MG based SIR at the impregnation ratio of 1 g Aliquat 336 / g-resin.

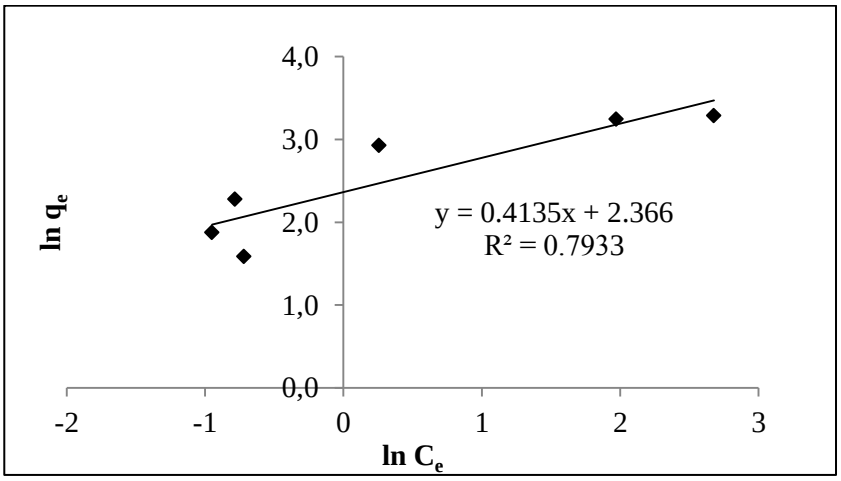


**Figure 3.10.** Linearized form of Freundlich isotherm for HP 2MG based SIR at the impregnation ratio of 1 g Aliquat 336 / g-resin.

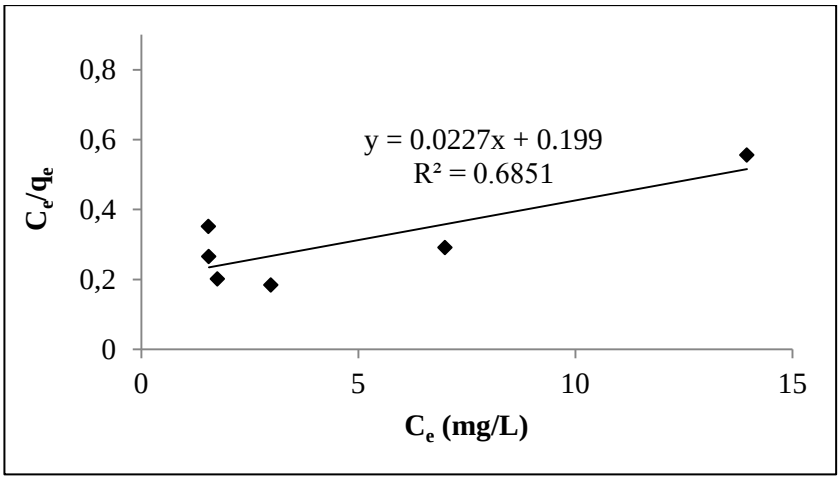


**Figure 3.11.** Linearized form of Langmuir isotherm for HP 2MG based SIR at the impregnation ratio of 2 g Aliquat 336 / g-resin.

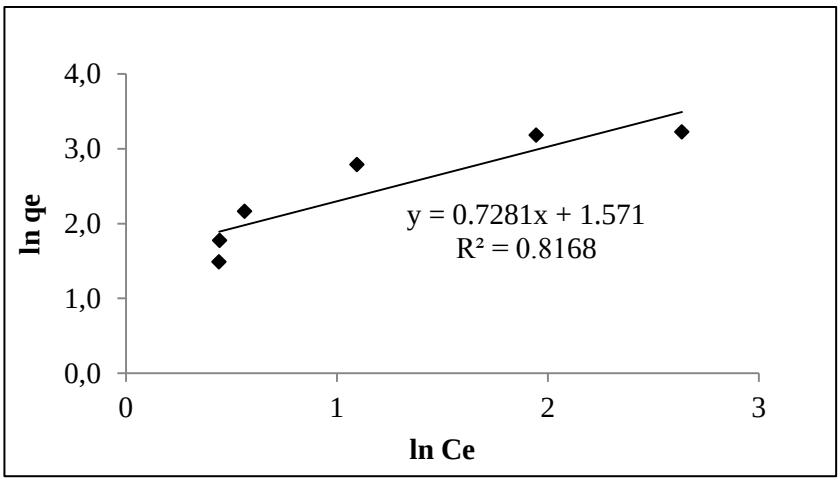


**Figure 3.12.** Linearized form of Freundlich isotherm for HP 2MG based SIR at the impregnation ratio of 2 g Aliquat 336 / g-resin.

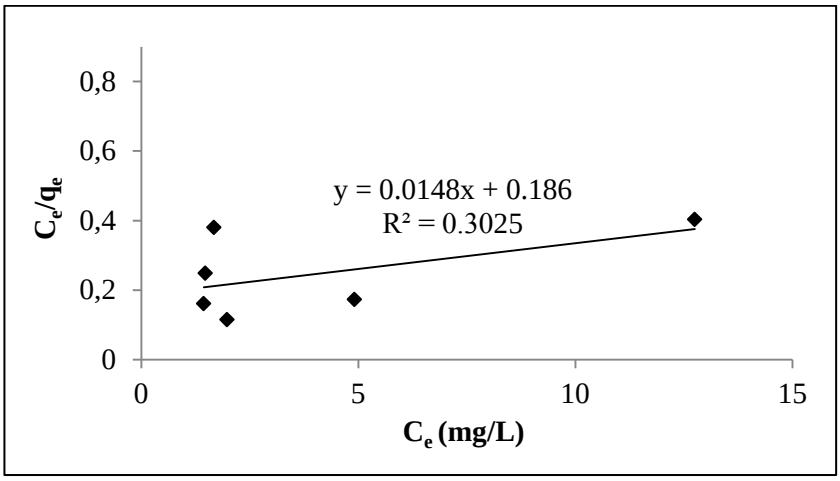


**Figure 3.13.** Linearized form of Langmuir isotherm for HP 2MG based SIR at the impregnation ratio of 3 g Aliquat 336 / g-resin.

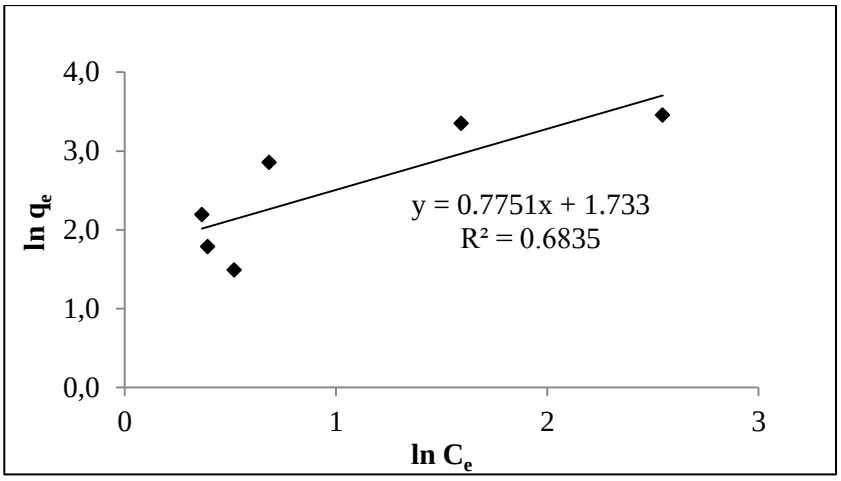


**Figure 3.14.** Linearized form of Freundlich isotherm for HP 2MG based SIR at the impregnation ratio of 3 g Aliquat 336 / g-resin.

The Freundlich model encompasses the heterogeneity of the adsorbent surface, the exponential distribution sites and their energies. On the other hand, the Langmuir model makes several assumptions, such as the adsorption energies are uniform and independent of surface coverage and complete coverage of the surface by a monolayer of adsorbate indicates maximum adsorption (Isa et al., 2008). Experimental data shows that at the impregnation ratio of 1g Aliquat 336/g-resin adsorbent surface is uniform, but when the impregnation ratio increases, adsorbent surface seems to loose its homogeneity. The correlation coefficients values were given in Table 3.1.

**Table 3.1.** Evaluation of Langmuir and Freundlich isotherms for HP 20 and HP 2MG based SIRs.

| **SIR** | **Impregnation Ratio** | **$R^2$** | |
|---|---|---|---|
| | | **Langmuir Isotherm** | **Freundlich Isotherm** |
| **HP 20 based SIR** | 1 g Aliquat 336/g-resin | **0.9896** | 0.9190 |
| | 2 g Aliquat 336/g-resin | 0.2273 | **0.8584** |
| | 3 g Aliquat 336/g-resin | 0.1630 | **0.7927** |
| **HP 2MG based SIR** | 1 g Aliquat 336/g-resin | **0.9890** | 0.7933 |
| | 2 g Aliquat 336/g-resin | 0.6851 | **0.8168** |
| | 3 g Aliquat 336/g-resin | 0.3025 | **0.6835** |

### 3.1.3 Kinetic Performans of SIRs

Figures 3.15 and 3.16 illustrate the relative concentration decrease of Cr(VI) versus time for both HP 20 and HP 2MG. The removal of Cr(VI) using HP 20 based SIR increased with time and reached the equilibrium in 120 min with a 85% Cr(VI) removal at the impregnation ratio of 1 g Aliquat 336/g-resin, in 30 min with a 99% Cr(VI) removal at the impregnation ratio of 2 g Aliquat 336/g-resin, in 30 min with a 90% Cr(VI) removal at the impregnation ratio of 3g Aliquat 336/g-resin. The removal of Cr(VI) using HP 2MG based SIR increased with time and reached the equilibrium in 180 min with a 95% Cr(VI) removal at the impregnation ratio of 1 g Aliquat 336/g-resin, in 60 min with a 99% Cr(VI) removal at the impregnation ratio of 2 g Aliquat 336/g-resin, in 60 min with a 98% Cr(VI) removal at the impregnation ratio of 3 g Aliquat 336/g-resin.

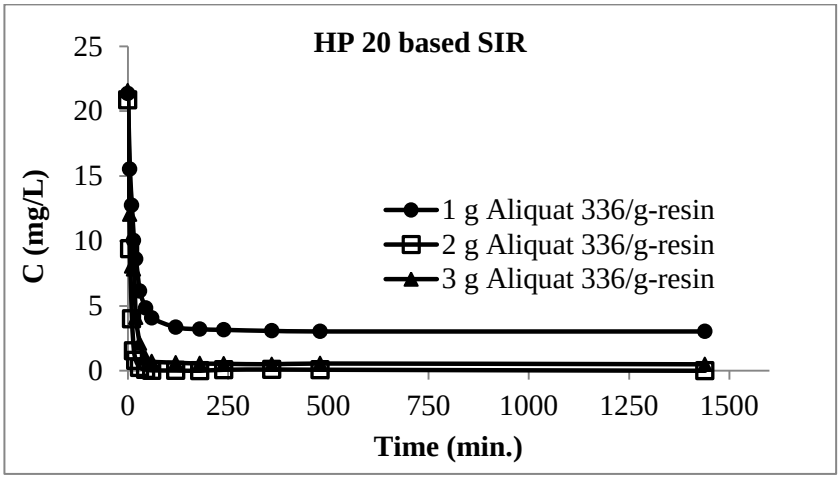


**Figure 3.15.** Effect of impregnation ratio on Cr(VI) sorption kinetics using HP 20 based SIRs.

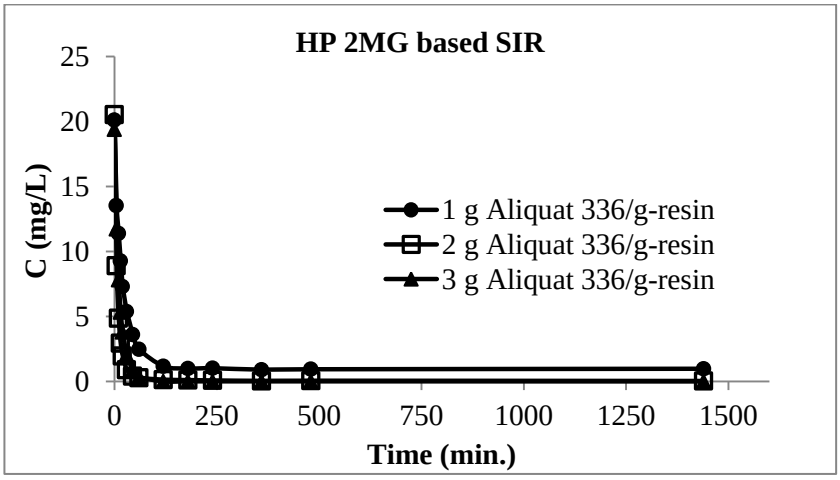


**Figure 3.16.** Effect of impregnation ratio on Cr(VI) sorption kinetics using HP 20 based SIRs.

### 3.1.4 Mathematical modeling

#### 3.1.4.1. Conventional kinetic models

When a single specie is considered to be adsorbed on a heterogeneous surface, the adsorption of a solute from an aqueous solution may follows reversible-first-order kinetics (Hosseini-Bandegharaei et al., 2010). The pseudo-first-order equation can be written as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (3.3)$$

After definite integration by applying the initial conditions qt =0 at t = 0 and $q_t = q_t$ at t = t, the equation becomes:

$$log(q_e - q_t) = logq_e - \frac{k_1}{2.303}t \qquad (3.4)$$

where $q_e$ and $q_t$ are the amounts of species sorbed at equilibrium and at time t (mg/g), respectively, and $k_1$ is the rate constant of pseudo-first-order sorption, ($min^{-1}$) (Hosseini-Bandegharaei et al., 2010; Ozacar and Sengil, 2004).

The pseudo-second-order model can be presented in the following form:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (3.5)$$

After defined integration by applying initial conditions, Eq. 3.5 becomes:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \qquad (3.6)$$

Eq. 3.6 can be rearranged to obtain a linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad (3.7)$$

where $k_2$ is the rate constant of pseudo-second-order sorption (g/mg min) (Hosseini-Bandegharaei et al., 2010; Ozacar and Sengil, 2004).

The kinetic data obtained were evaluated with pseudo-first-order and pseudo-second-order kinetics models using equations that were given above (Eqs. 3.4 and 3.7). The graphs of log(qe-qt) versus t and t/qt versus t were plotted for pseudo first-order and pseudo second-order kinetic models, respectively, for the experiments done with HP 20 and HP 2MG based SIRs to determine the correlation coefficients (Figure 3.17-3.28).

The correlation coefficients of pseudo-first-order kinetics ($R^2$) are greater than those of pseudo-second-order kinetics for HP 20 based SIR prepared at the impregnation ratio of 2 g Aliquat 336/g-resin and HP 2MG based SIR prepared at the impregnation ratio of 1 g Aliquat 336/g-resin. Although, pseudo-second-order kinetic model was better for other impregnation ratios of HP 20 and HP 2MG based SIRs. The correlation coefficients were given Table 3.2.

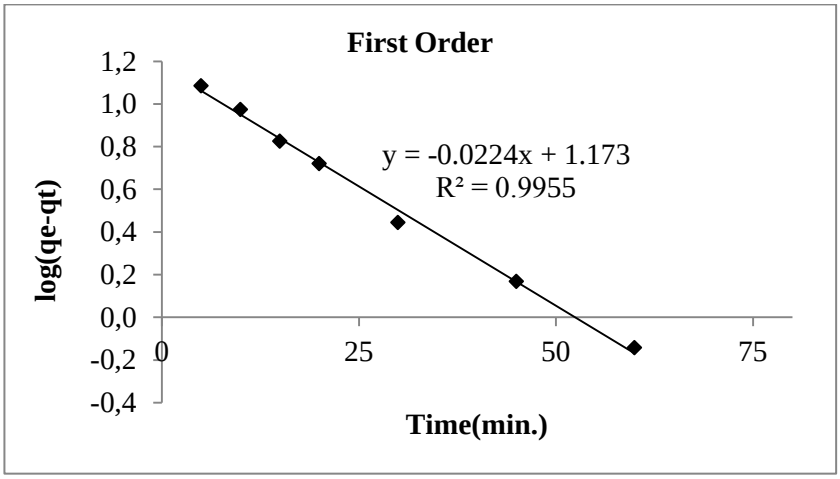


**Figure 3.17.** Evaluation of kinetic data using pseudo-first-order kinetic model for HP 20 based SIR prepared at the impregnation ratio of 1 g Aliquat 336/g-resin.

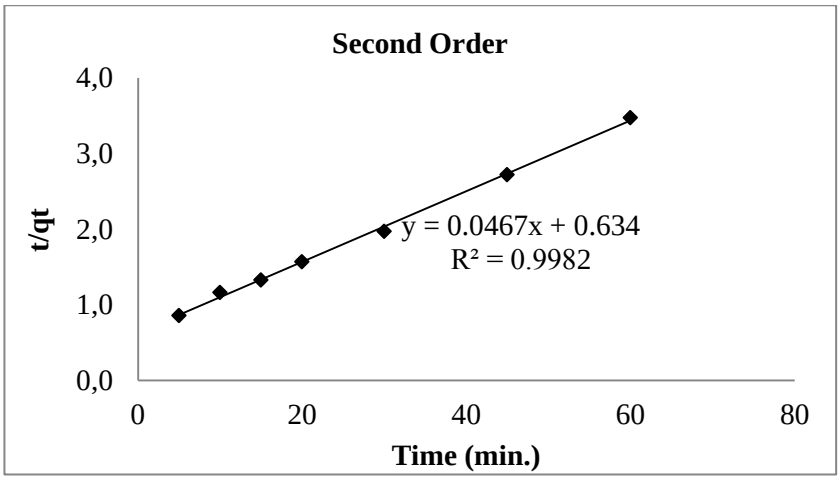


**Figure 3.18.** Evaluation of kinetic data using pseudo-second-order kinetic model for HP 20 based SIR prepared at the impregnation ratio of 1 g Aliquat 336/g-resin.

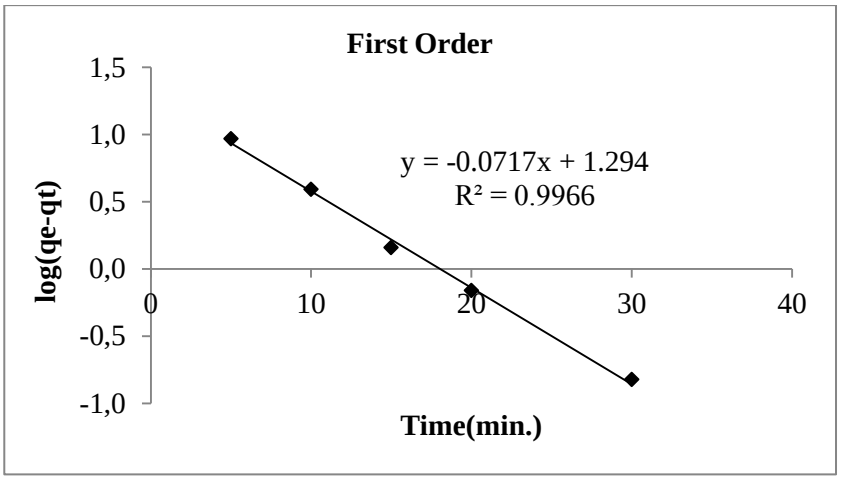


**Figure 3.19.** Evaluation of kinetic data using pseudo-first-order kinetic model for HP 20 based SIR prepared at the impregnation ratio of 2 g Aliquat 336/g-resin.

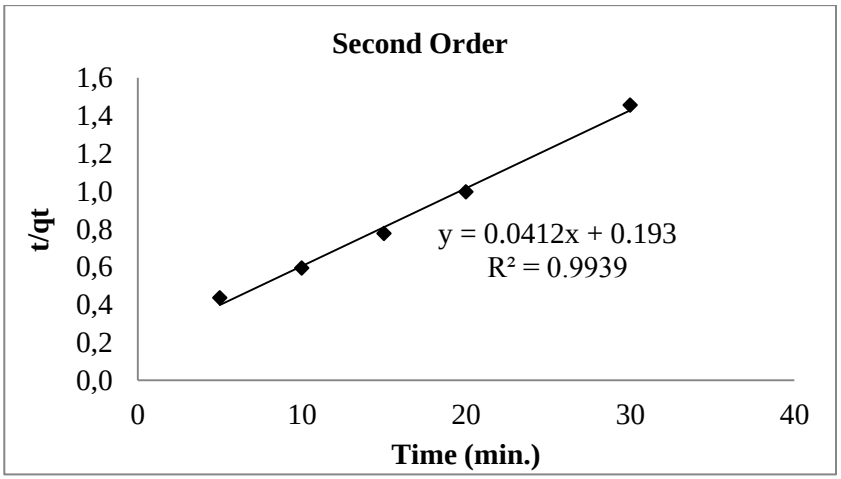


**Figure 3.20.** Evaluation of kinetic data using pseudo-second-order kinetic model for HP 20 based SIR prepared at the impregnation ratio of 2 g Aliquat 336/g-resin.

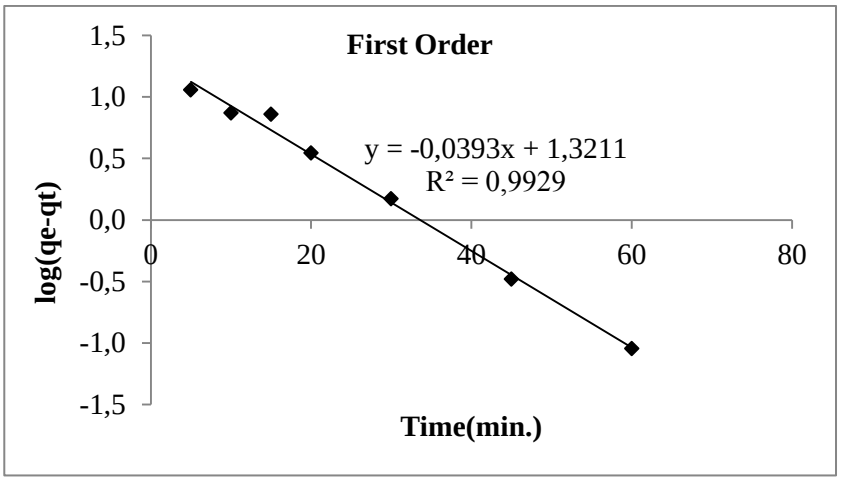


**Figure 3.21.** Evaluation of kinetic data using pseudo-first-order kinetic model for HP 20 based SIR prepared at the impregnation ratio of 3 g Aliquat 336/g-resin.

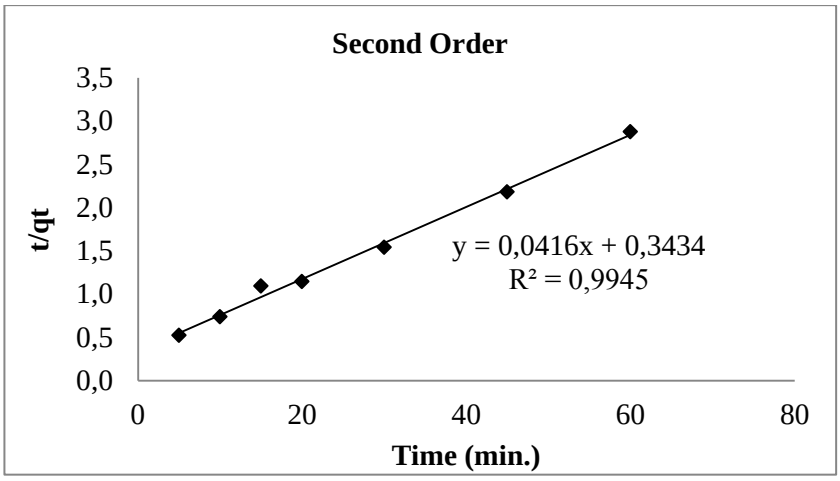


**Figure 3.22.** Evaluation of kinetic data using pseudo-second-order kinetic model for HP 20 based SIR prepared at the impregnation ratio of 3 g Aliquat 336/g-resin.

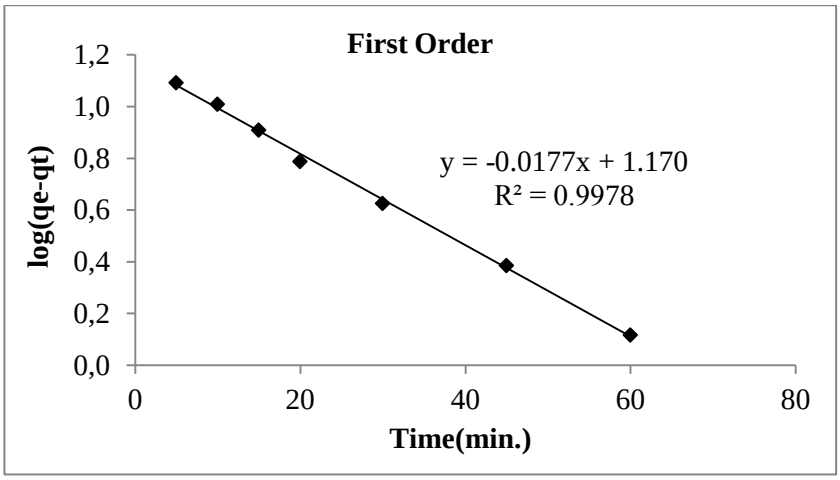


**Figure 3.23.** Evaluation of kinetic data using pseudo-first-order kinetic model for HP 2MG based SIR prepared at the impregnation ratio of 1 g Aliquat 336/g-resin.

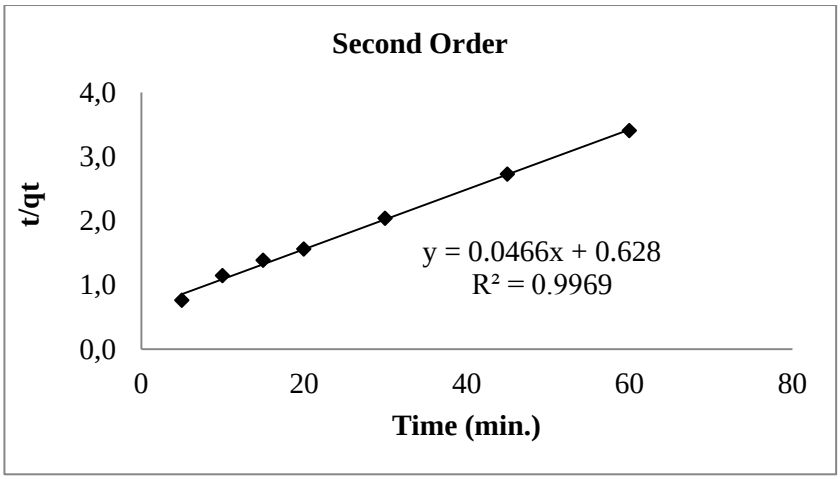


**Figure 3.24.** Evaluation of kinetic data using pseudo-second-order kinetic model for HP 2MG based SIR prepared at the impregnation ratio of 1 g Aliquat 336/g-resin.

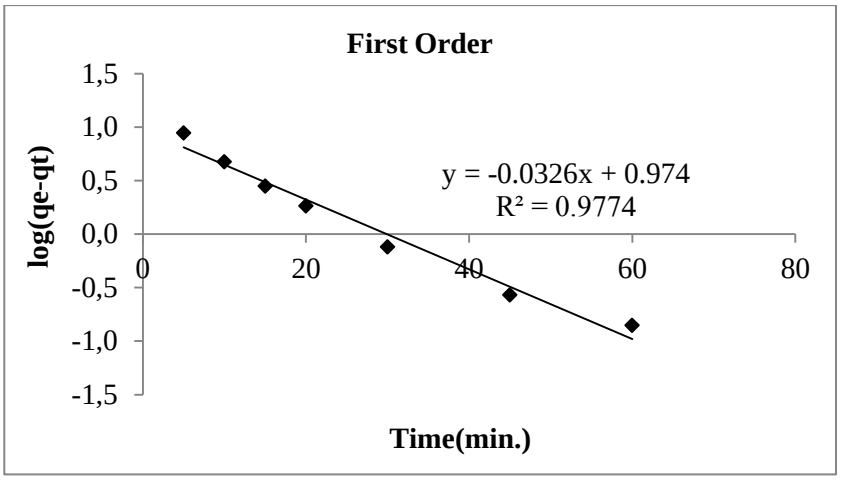


**Figure 3.25.** Evaluation of kinetic data using pseudo-first-order kinetic model for HP 2MG based SIR prepared at the impregnation ratio of 2 g Aliquat 336/g-resin.

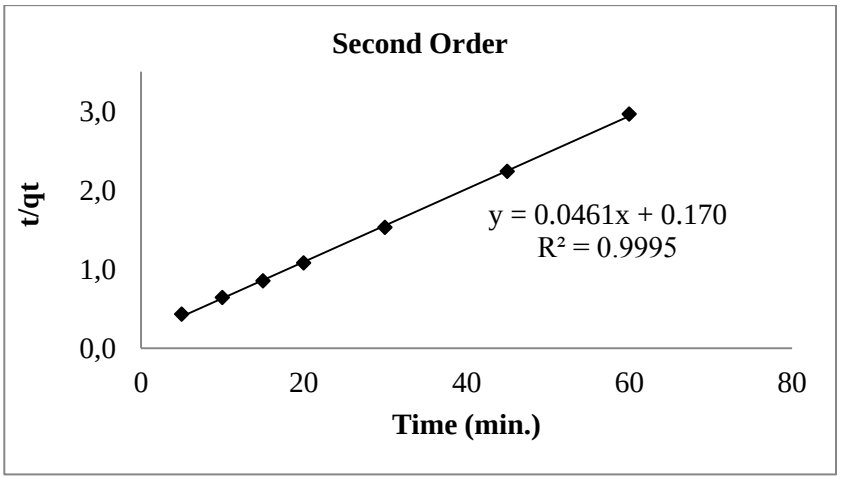


**Figure 3.26.** Evaluation of kinetic data using pseudo-second-order kinetic model for HP 2MG based SIR prepared at the impregnation ratio of 2 g Aliquat 336/g-resin.

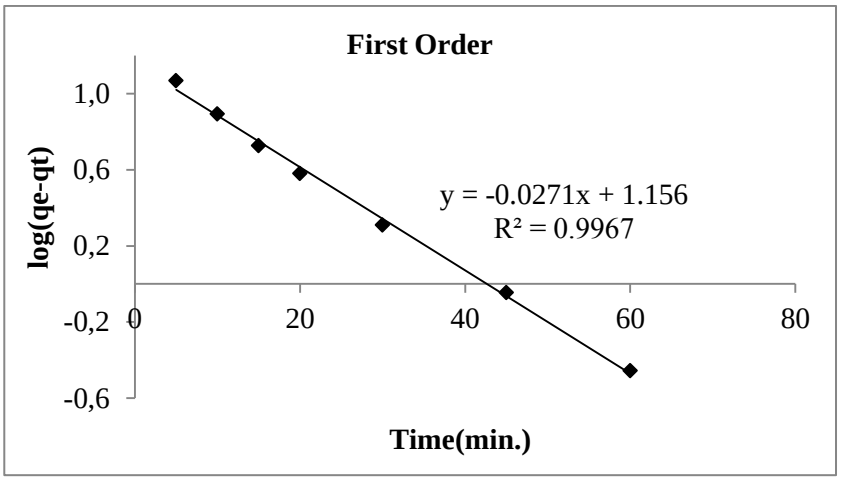


**Figure 3.27.** Evaluation of kinetic data using pseudo-first-order kinetic model for HP 2MG based SIR prepared at the impregnation ratio of 3 g Aliquat 336/g-resin.

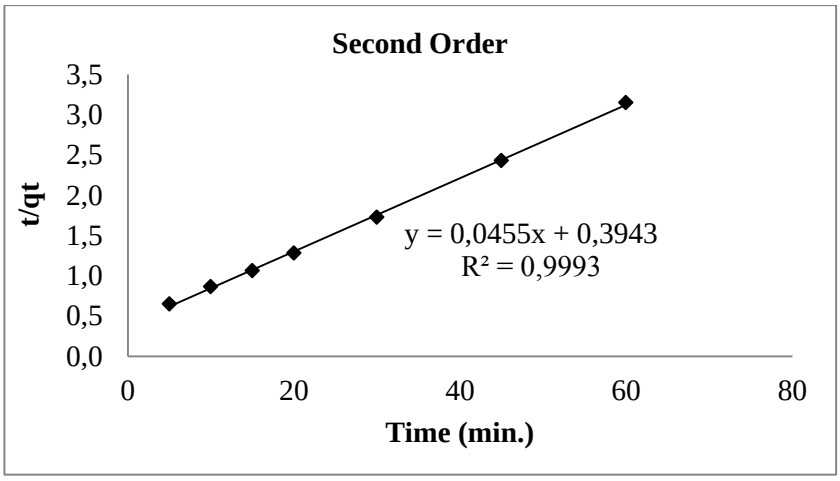


**Figure 3.28.** Evaluation of kinetic data using pseudo-second-order kinetic model for HP 2MG based SIR prepared at the impregnation ratio of 3 g Aliquat 336/g-resin.

**Table 3.2.** Evaluation of sorption kinetic data obtained using conventional kinetic modeling for HP 20 and HP 2MG based SIRs.

| SIR | Impregnation Ratio | $R^2$ | |
|---|---|---|---|
| | | Pseudo-first-order | Pseudo-second-order |
| HP 20 based | 1 g Aliquat 336/g-resin | 0.9955 | **0.9982** |
| | 2 g Aliquat 336/g-resin | **0.9966** | 0.9939 |
| | 3 g Aliquat 336/g-resin | 0.9929 | **0.9945** |
| HP 2MG based | 1 g Aliquat 336/g-resin | **0.9978** | 0.9969 |
| | 2 g Aliquat 336/g-resin | 0.9774 | **0.9995** |
| | 3 g Aliquat 336/g-resin | 0.9967 | **0.9993** |

## 3.1.4.2 Diffusional and reaction models

Rates of the interactions are highly dependent on the materials' internal structure that is in contrary to kinetics in homogeneous media, in systems including fine powders, and to kinetics of most of the surface processes (Zagorodni, 2007).

Ion exchange rates can be controlled by rates of actual chemical reactions, however, control by diffusion processes is a more common case. Moreover, many ion exchange interactions do not involve any direct chemical reactions and, hence, the overall process is controlled solely by the diffusion which, in turn, is defined by the material structure. Besides the microstructure, macroshape of the material (size of the beads, layers, membranes, etc.) also influences apparent rates of ion exchange. This is because larger pieces could require more time for the process to

be completed if the rate is limited by diffusion through bulk of the material. Thus, kinetic approaches are very specific for ion exchange materials (Zagorodni, 2007).

The kinetic study data were evaluated by using two approaches. The first one is based on Fick's first law of integration of material balance for infinite solution volume (ISV). The second method uses the unreacted core model (UCM) in which ion exchange is treated as a heterogeneous reaction. According to UCM, reaction first occurs at the outer skin of the particle, then within a zone moving into the particle through the unreacted core. Kinetic models developed for spherical particles to specify the rate-determining steps were given in Table 3.3 (Badruk et al., 1999).

**Table 3.3.** Diffusional and reaction models (Badruk et al., 1999).

| Model | Equation | Rate-determining step |
|---|---|---|
| ISV | $F(X)=-\ln(1-X)=K_{1i}t$ where $K_{1i}=3DC/r_o\delta C_r$ | Film diffusion |
| ISV | $F(X)=-\ln(1-X^2)=kt$ where $k=D_r\pi^2/r_o^2$ | Particle diffusion |
| UCM | $F(X)=X=(3C_{Ao}K_{mA}/a_{ro}C_{so})t$ | Liquid film |
| UCM | $F(X)=3-3(1-X)^{2/3}-2X=(6D_{eR}C_{Ao}/a_{ro}^2C_{so})t$ | Reacted layer |
| UCM | $F(X)=1-(1-X)^{1/3}=(k_sC_{A0}/a_{ro}C_{so})t$ | Chemical reaction |

The kinetic data obtained were also evaluated with diffusional and reaction models for HP 20 and HP 2MG based SIRs (Figures 3.29-3.40).

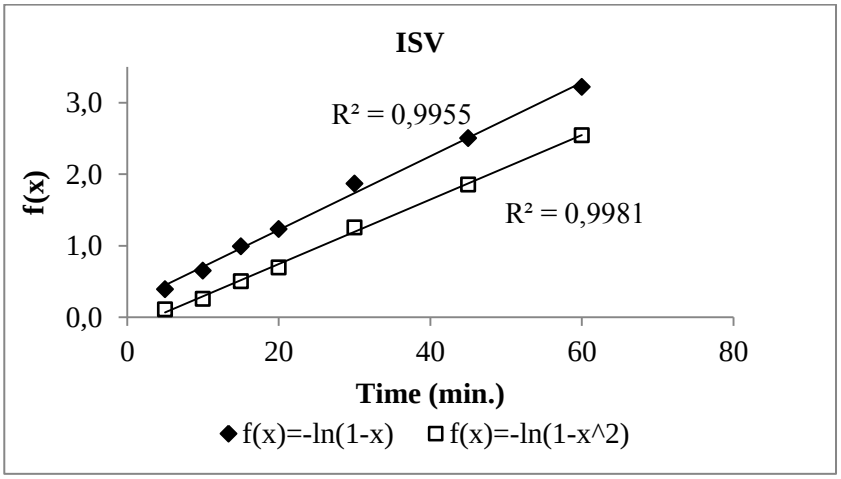


**Figure 3.29.** Evaluation of kinetic data using infinite solution volume model (ISV) for HP 20 based SIR prepared at the impregnation ratio of 1 g Aliquat 336/g-resin.

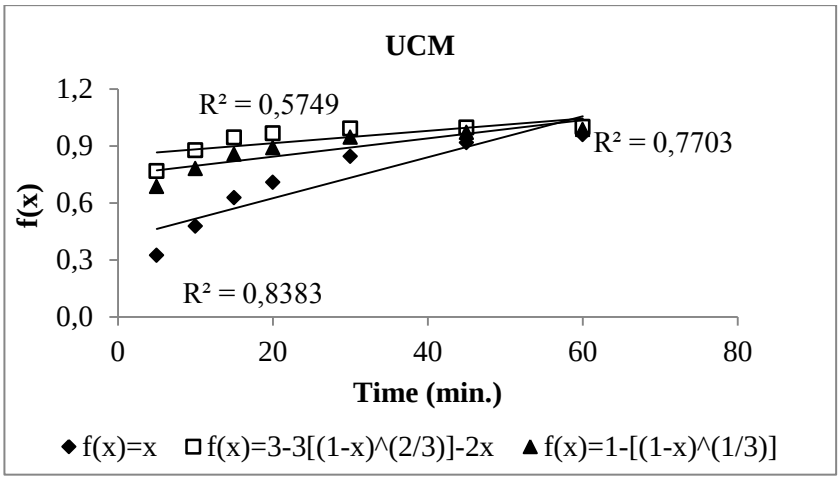


**Figure 3.30.** Evaluation of kinetic data using unreacted core model (UCM) for HP 20 based SIR prepared at the impregnation ratio of 1 g Aliquat 336/g-resin.

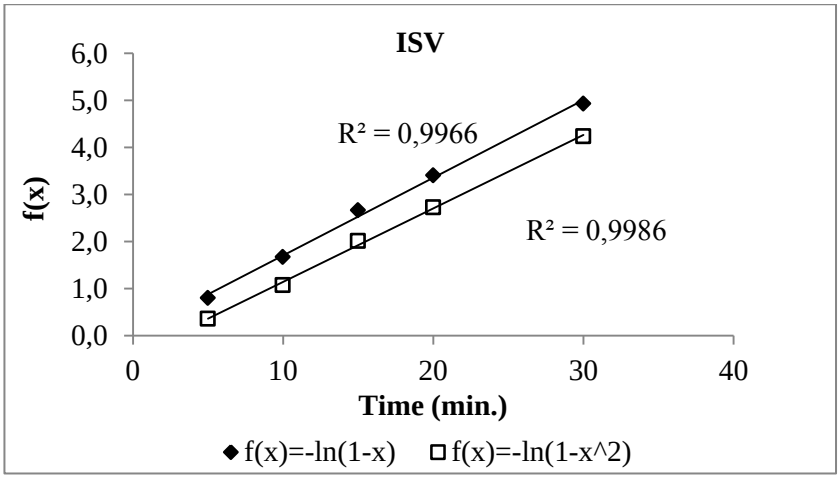


**Figure 3.31.** Evaluation of kinetic data using infinite solution volume model (ISV) for HP 20 based SIR prepared at the impregnation ratio of 2 g Aliquat 336/g-resin.

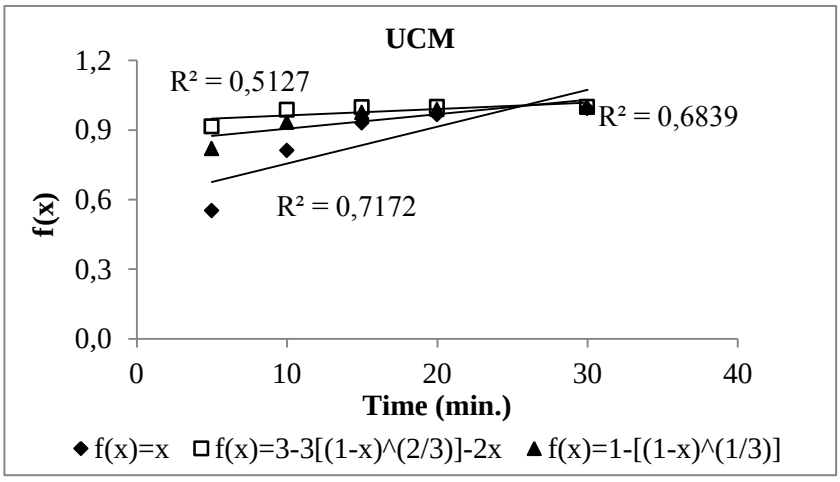


**Figure 3.32.** Evaluation of kinetic data using unreacted core model (UCM) for HP 20 based SIR prepared at the impregnation ratio of 2 g Aliquat 336/g-resin.

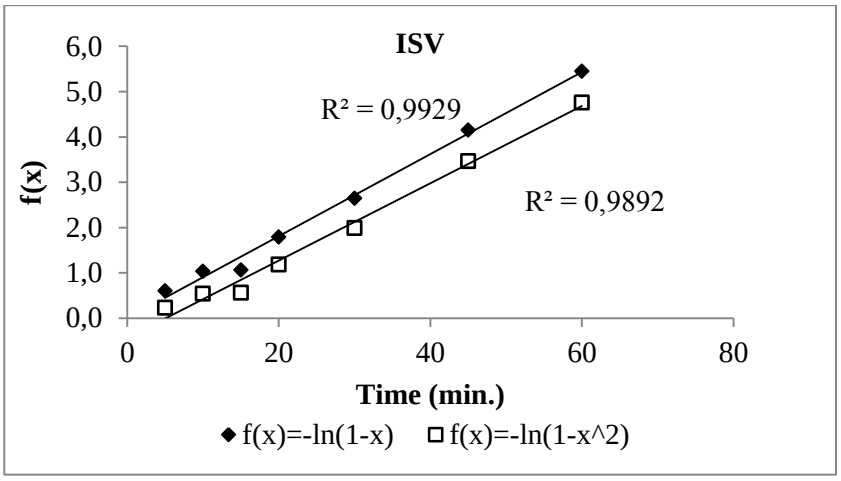


**Figure 3.33.** Evaluation of kinetic data using infinite solution volume model (ISV) for HP 20 based SIR prepared at the impregnation ratio of 3 g Aliquat 336/g-resin.

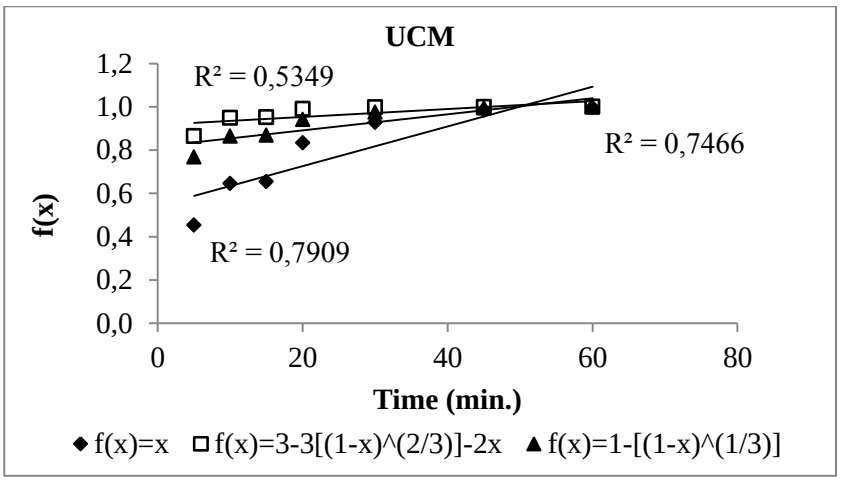


**Figure 3.34.** Evaluation of kinetic data using unreacted core model (UCM) for HP 20 based SIR prepared at the impregnation ratio of 3 g Aliquat 336/g-resin.

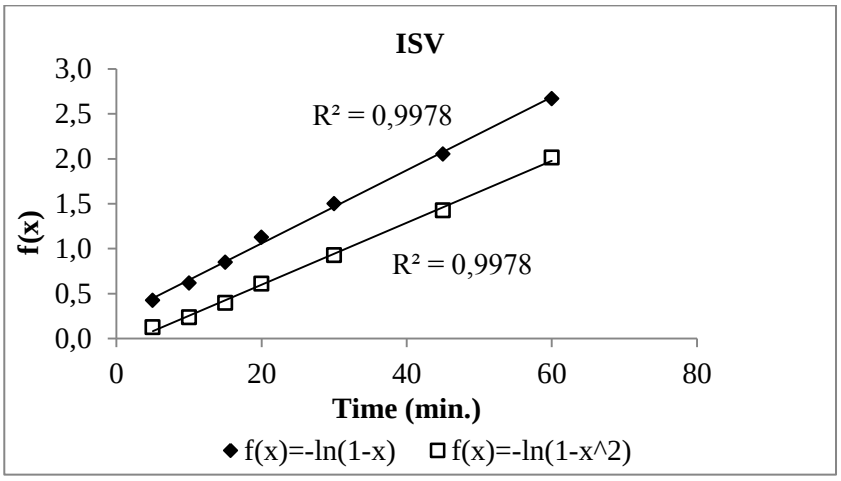


**Figure 3.35.** Evaluation of kinetic data using infinite solution volume model (ISV) for HP 2MG based SIR prepared at the impregnation ratio of 1 g Aliquat 336/g-resin.

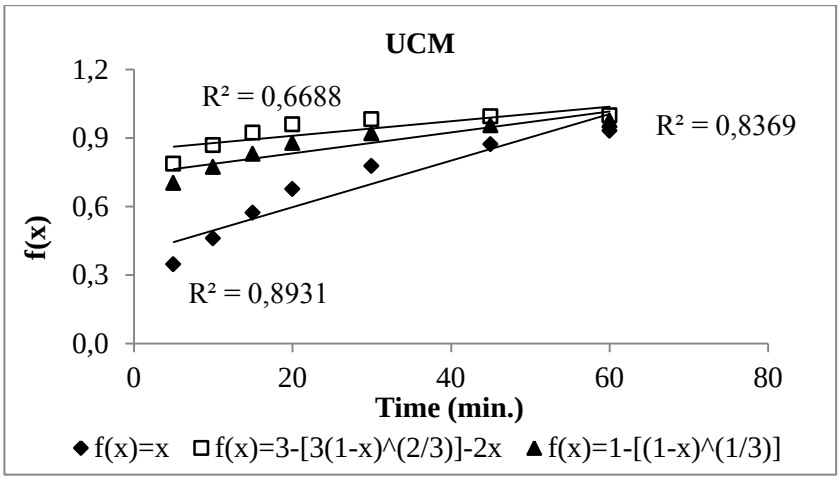


**Figure 3.36.** Evaluation of kinetic data using unreacted core model (UCM) for HP 2MG based SIR prepared at the impregnation ratio of 1 g Aliquat 336/g-resin.

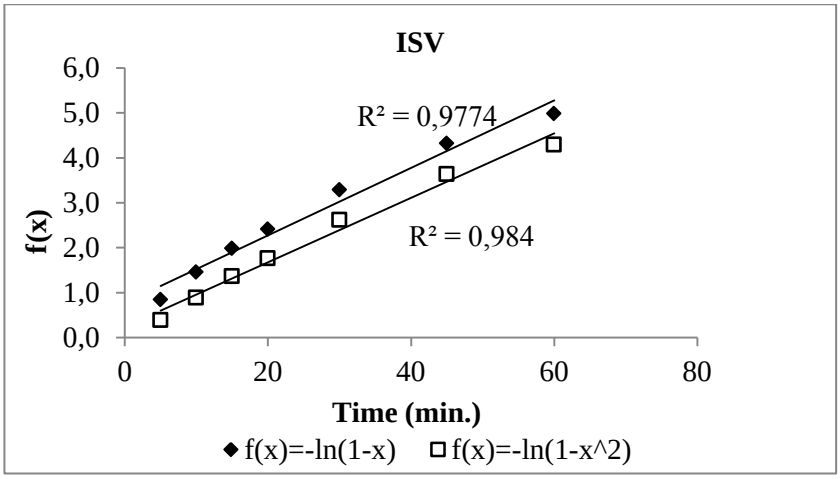


**Figure 3.37.** Evaluation of kinetic data using infinite solution volume model (ISV) for HP 2MG based SIR prepared at the impregnation ratio of 2 g Aliquat 336/g-resin.

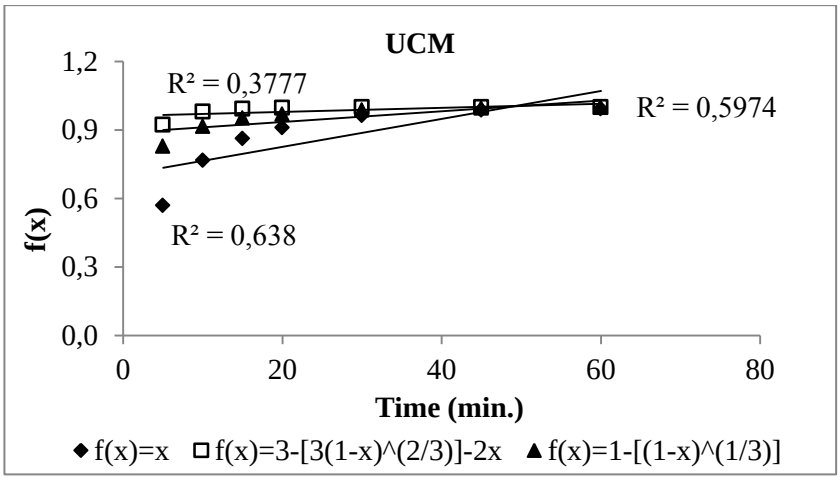


**Figure 3.38.** Evaluation of kinetic data using unreacted core model (UCM) for HP 2MG based SIR at the impregnation ratio of 2 g Aliquat 336 / g-resin.

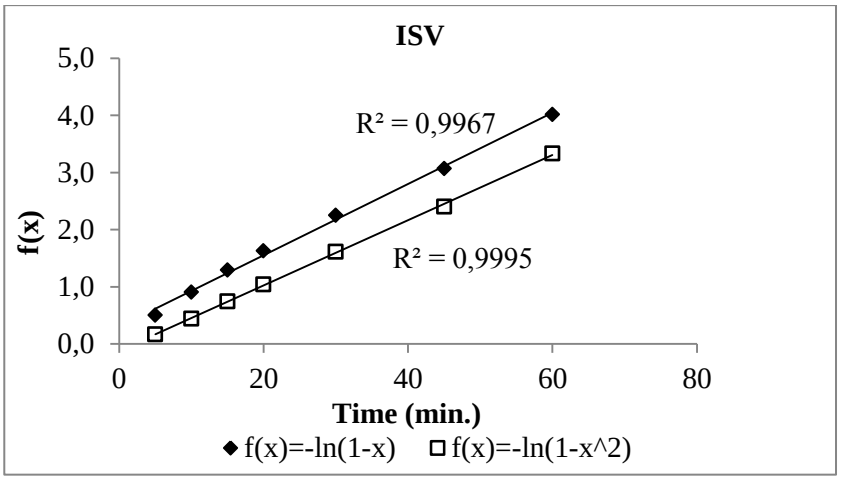


**Figure 3.39.** Evaluation of kinetic data using infinite solution volume model (ISV) for HP 2MG based SIR at the impregnation ratio of 3 g Aliquat 336 / g-resin.

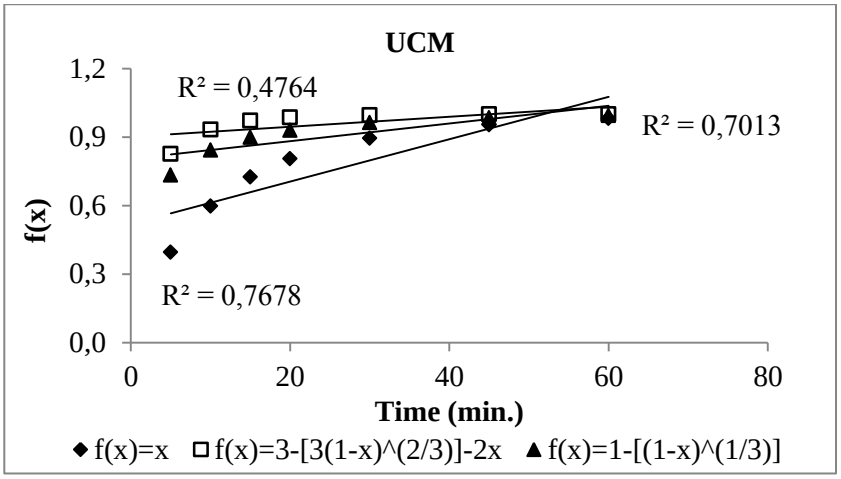


**Figure 3.40.** Evaluation of kinetic data using unreacted core model (UCM) for HP 2MG based SIR at the impregnation ratio of 3 g Aliquat 336/g-resin.

The maximum correlation coefficients for the linear models show that the rate is particle diffusion controlled according to ISV models for HP 20 based SIR at the impregnation ratios 1 g Aliquat 336/g-resin and 2 g Aliquat 336/g-resin, film diffusion controlled at the impregnation ratio of 3g Aliquat 336/ g-resin. The rate is liquid film controlled according to UCM models for HP 20 based SIRs at the impregnation ratios of 1 g Aliquat 336/g-resin, 2 g Aliquat 336/g-resin and 3 g Aliquat 336/ g-resin. For HP 2MG based SIRs at the impregnation ratios of 1 g Aliquat 336/g-resin, 2 g Aliquat 336/g-resin and 3 g Aliquat 336/ g-resin, the rate is particle diffusion controlled mostly according to ISV models. The rate is liquid film controlled according to UCM models for HP 2MG based SIRs at the impregnation ratios of 1 g Aliquat 336/g-resin, 2 g Aliquat 336/g-resin and 3 g Aliquat 336/ g-resin. Table 3.4 shows the linear correlation coefficients obtained from the plots of F(X) function versus time as shown in (Figures 3.29-3.40).

**Table 3.4.** Evaluation of sorption kinetic data obtained using diffusional and reaction models for SIRs.

| SIR | Impregnation Ratio | $R^2$ | | | | |
|---|---|---|---|---|---|---|
| | | ISV | | UCM | | |
| | | Film diffusion $-\ln(1-X)$ | Particle diffusion $-\ln(1-X^2)$ | Liquid film X | Reacted layer $3-3(1-X)^{2/3}-2X$ | Chemical reaction $1-(1-X)^{1/3}$ |
| HP 20 Based | 1 g Aliquat 336 /g-resin | 0.9955 | **0.9981** | **0.8931** | 0.5749 | 0.7703 |
| | 2 g Aliquat 336 /g-resin | 0.9966 | **0.9986** | **0.7172** | 0.5127 | 0.6839 |
| | 3 g Aliquat 336 /g-resin | **0.9929** | 0.9892 | **0.7909** | 0.5349 | 0.7646 |
| HP 2MG Based | 1 g Aliquat 336 /g-resin | **0.9978** | **0.9978** | **0.8931** | 0.6688 | 0.8369 |
| | 2 g Aliquat 336 /g-resin | 0.9774 | **0.9840** | **0.638** | 0.3777 | 0.5974 |
| | 3 g Aliquat 336 /g-resin | 0.9967 | **0.9995** | **0.7678** | 0.4764 | 0.7013 |

## 3.2 Column-mode Sorption of Cr(VI) by SIRs

The breakthrough and elution profiles of Cr(VI) for HP 20 based SIRs were given in Figures 3.41 and 3.42. For HP 2MG based SIRs, they were given in Figures 3.43 and 3.44.

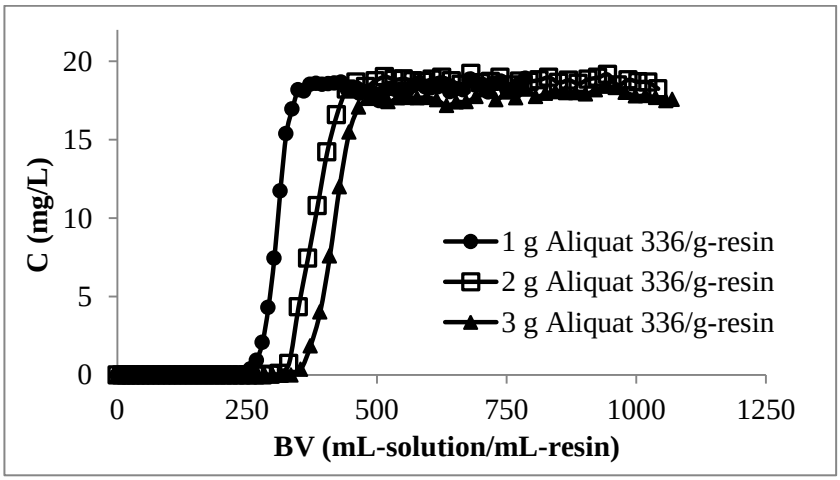


**Figure 3.41.** Breakthrough profiles of Cr(VI) by HP 20 based SIRs prepared at different impregnation ratios (SV 15 $h^{-1}$).

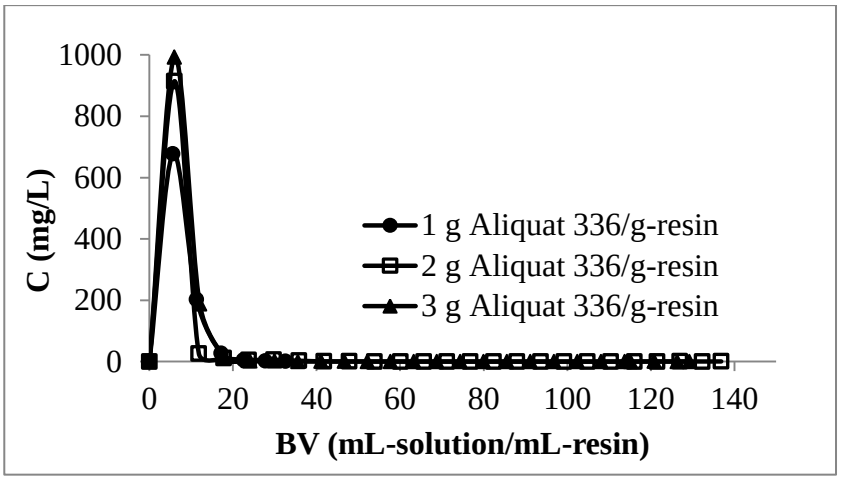


**Figure 3.42.** Elution profiles of Cr(VI) by HP 20 based SIRs prepared at different impregnation ratios (SV 5 $h^{-1}$).

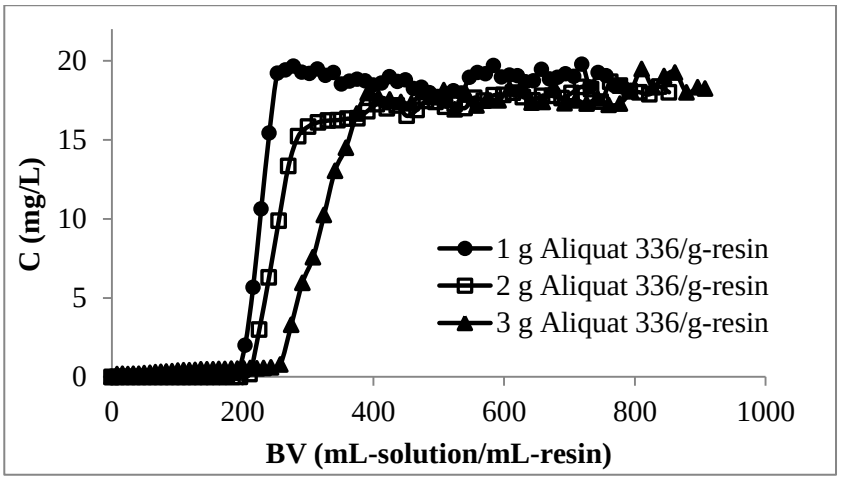


**Figure 3.43.** Breakthrough profiles of Cr(VI) by HP 2MG based SIRs prepared at different impregnation ratios (SV 15 $h^{-1}$).

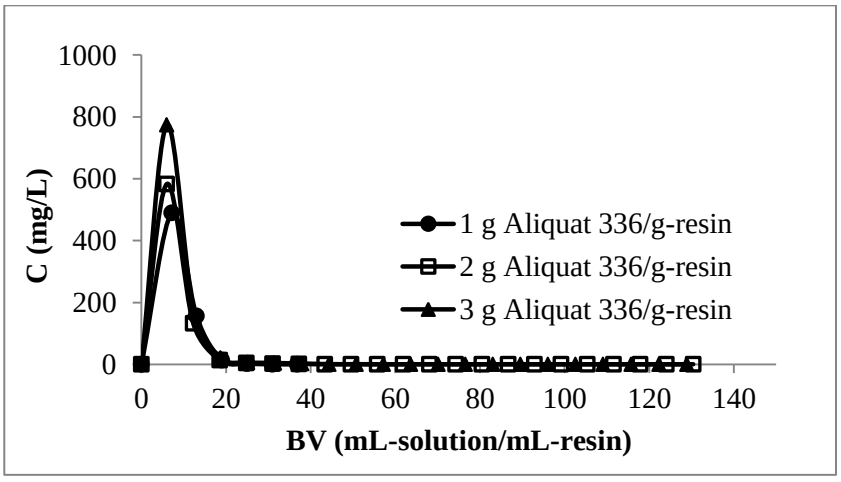


**Figure 3.44.** Elution profiles of Cr(VI) by HP 2MG based SIRs prepared at different impregnation ratios at (SV 5 $h^{-1}$).

Data of column study were given in Table 3.5. Breakthrough capacities were calculated by accepting the breakthrough point as the concentration just before 1.0 mg Cr(VI)/L. Relating to the total and breakthrough capacities, the best column performance was observed with the SIRs prepared at impregnation ratio of 3 g Aliquat 336/g-resin. When HP 20 and HP 2MG polymer matrix were compared, the total and breakthrough capacities of HP 20 based SIRs were higher than those of HP 2MG based SIRs. Swelling of HP 2MG is higher than that of HP 20 as informed in Table 2.1. Higher swelling causes decrease of functional groups in unit volume. That is also result of hydrophilic character of HP 2MG (methacrylic) and hydrophobic character of HP 20 (styrene-divinylbenzene).

**Table 3.5.** Results of column studies using HP 20 and HP 2MG based SIRs.

| **Polymer Matrix and Impregnation Ratio** | | **Breakthrough capacity (mg Cr(VI) /mL resin)** | **Total capacity (mg Cr(VI) /mL resin)** | **Total capacity (mg Cr(VI) /g resin)** | **Elution efficiency (%)** | **Column utilization (%)** |
|---|---|---|---|---|---|---|
| **HP 20** | **1 g Aliquat 336/ g-resin** | 5.02 | 5.80 | 34.22 | 89 | 87 |
| | **2 g Aliquat 336/ g-resin** | 6.08 | 6.73 | 39.71 | 82 | 90 |
| | **3 g Aliquat 336/ g-resin** | 6.42 | 7.49 | 44.19 | 94 | 93 |
| **HP 2MG** | **1 g Aliquat 336/ g-resin** | 3.55 | 3.92 | 23.52 | 99 | 90 |
| | **2 g Aliquat 336/ g-resin** | 3.72 | 4.54 | 27.24 | 99 | 82 |
| | **3 g Aliquat 336/ g-resin** | 4.44 | 5.32 | 31.92 | 100±14 | 84 |
| (0.3 g HP 20 = 0.9 mL, 0.3 g HP 2MG = 0.9 mL) | | | | | | |

## 3.3 Removal of Cr(VI) by Ion Exchange Resins

Cr(VI) removal studies were investigated for P(ClAPTA) and P(ClVBTA) resins that were synthesized in the laboratory of Concepcion University and commercial Amberlite IRA-400 resin. The performans of sorption of the synthesized and commercial resins were compared using batch-mode studies.

### 3.3.1 Characterisation of ion exchange resins

Figure 3.45 shows the IR spectra of P(ClVBTA) and P(ClAPTA) resins. The following main characteristic absorption peaks can be identified: for P(ClVBTA) the spectrum shows peaks at 3017 $cm^{-1}$ (C-H aromatic ring, st), 2915

$cm^{-1}$ (C-H, st), 1661 $cm^{-1}$ (aromatic ring), 1480 $cm^{-1}$ ($-N^{+}(CH_3)_3$), while for P(ClAPTA) the observed the peaks are at 2933 $cm^{-1}$ (C-H alifatic), 1642 $cm^{-1}$ (C=O), 1483 $cm^{-1}$ ($-N^{+}(CH_3)_3$). The presence of these vibrational bands confirms that structure possesses the functional groups of monomer used for the syntheses.

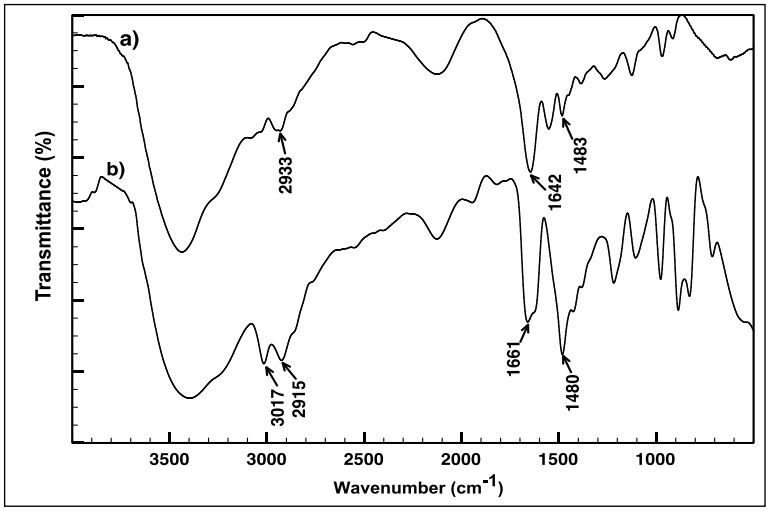


**Figure 3.45.** FT-IR spectra of ion exchange resins synthesized (a) P(ClAPTA) and (b) P(ClVBTA).

## 3.3.2 Effect of pH on the sorption of Cr(VI)

Effect of pH on the sorption of Cr(VI) was investigated for P(ClAPTA). The results show that Cr(VI) sorption on P(ClAPTA) and P(ClVBTA) resins depend on pH. As seen from Figure 3.46, the highest removal of Cr(VI) was observed at pH 6-10 for each resin. In the further studies, pH 9 was accepted as optimum pH.

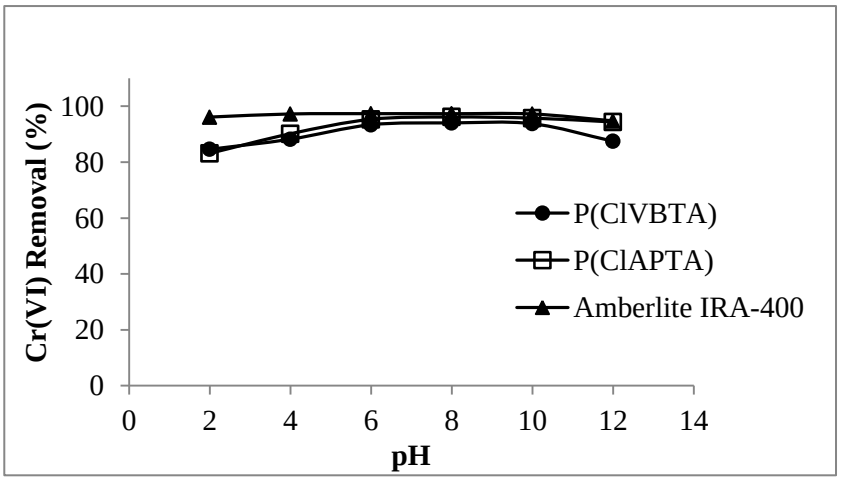


**Figure 3.46.** Effect of pH on the removal of Cr(VI) by P(ClAPTA), P(ClVBTA) and Amberlite IRA-400.

### 3.3.3 Equilibrium studies

Equilibrium data were obtained for Cr(VI) sorption by P(ClVBTA), P(ClAPTA) and Amberlite IRA-400 at pH 9. It was found that the increase of temperature does not effect it as seen from Figures 3.47-3.49 for P(ClVBTA), P(ClAPTA) and Amberlite IRA-400 respectively.

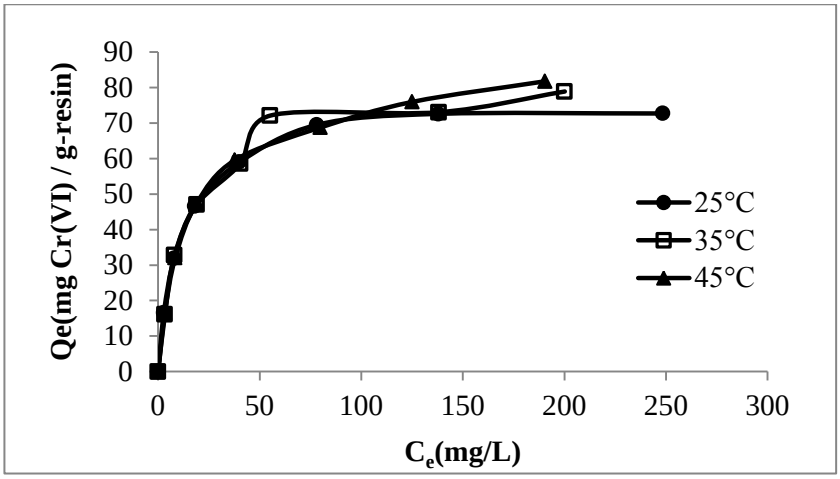


**Figure 3.47.** Qe vs. Ce for P(ClVBTA) as a function of temperature.

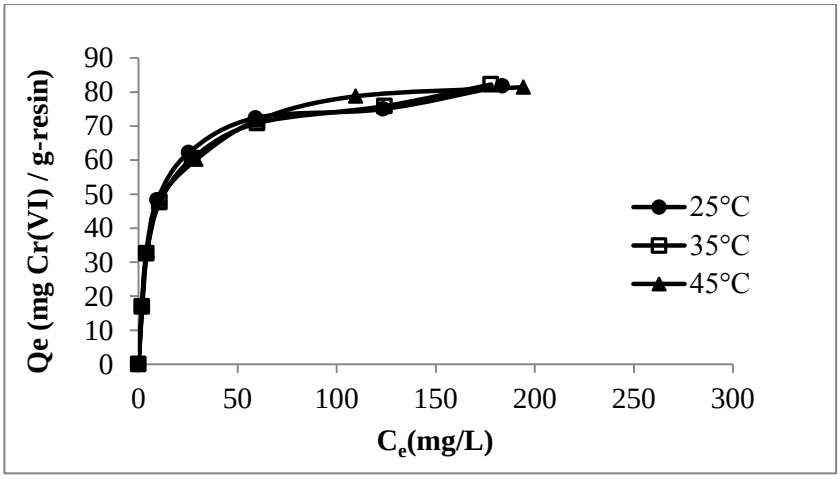


**Figure 3.48.** Qe vs. Ce for P(ClAPTA) as a function of temperature.

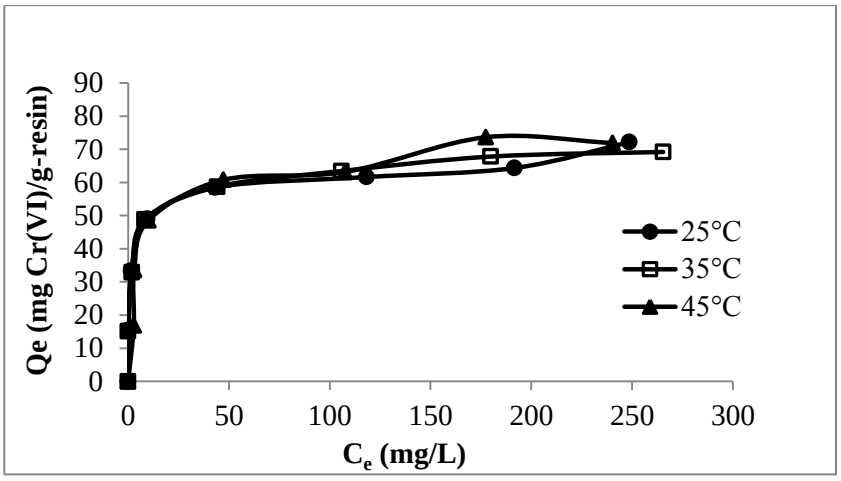


**Figure 3.49.** Qe vs. Ce for Amberlite IRA-400 as a function of temperature.

In addition, the equilibrium data were evaluated using Langmuir and Freundlich adsorption isotherm models.

As seen from the plots of Langmuir and Freundlich isotherms (Figures 3.50 -3.67), the equilibrium data fit well to Langmuir isotherm model for P(ClVBTA), P(ClAPTA) and Amberlite IRA-400 resins at each temperature. The correlation coefficient values were given in Table 3.6.

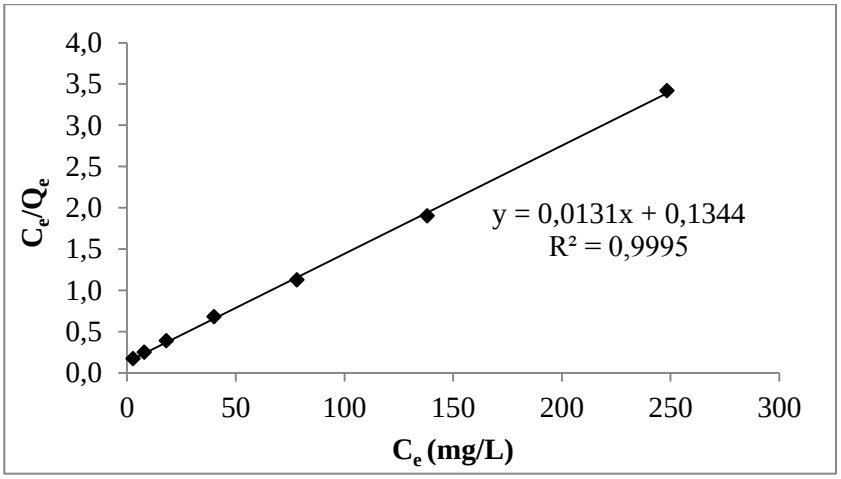


**Figure 3.50.** Linearized form of Langmuir isotherm for P(ClVBTA) at 25°C.

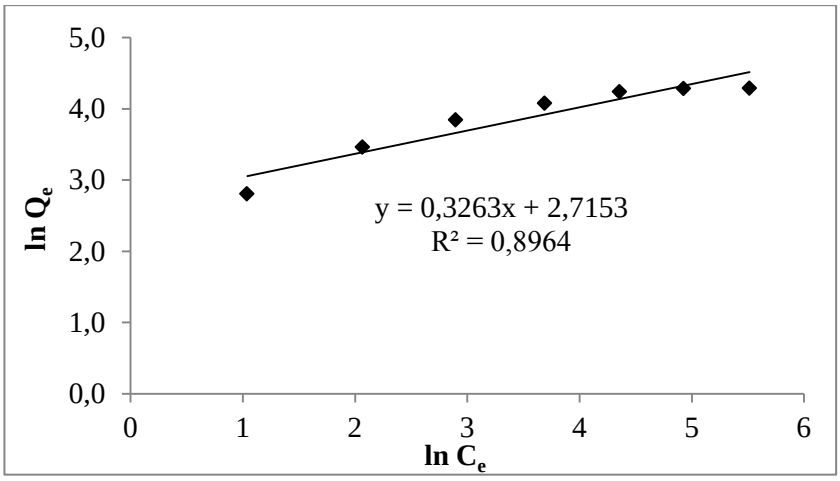


**Figure 3.51.** Linearized form of Freundlich isotherm for P(ClVBTA) at 25°C.

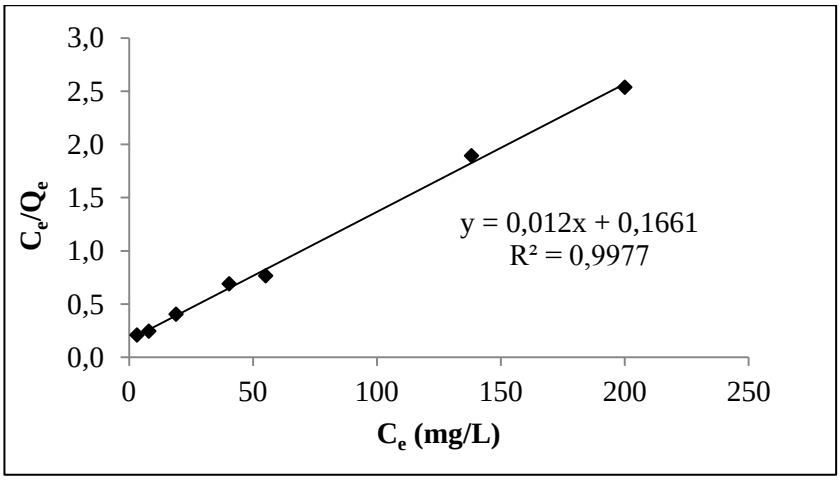


**Figure 3.52.** Linearized form of Langmuir isotherm for P(ClVBTA) at 35°C.

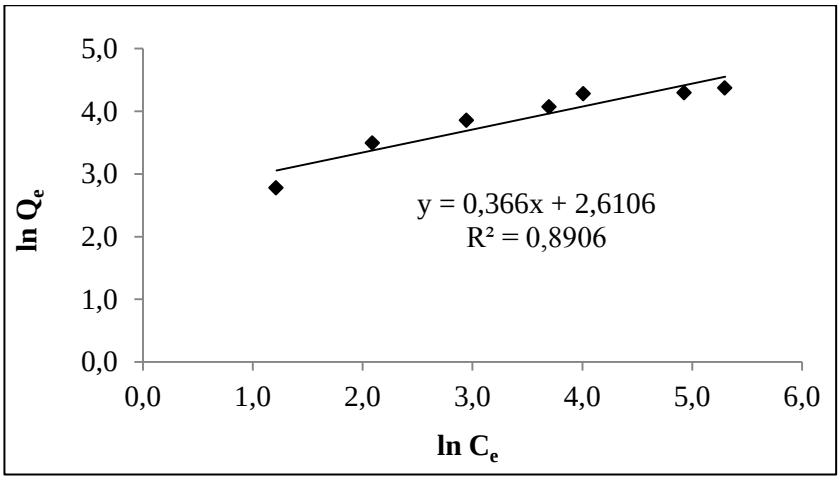


**Figure 3.53.** Linearized form of Freundlich isotherm for P(ClVBTA) at 35°C.

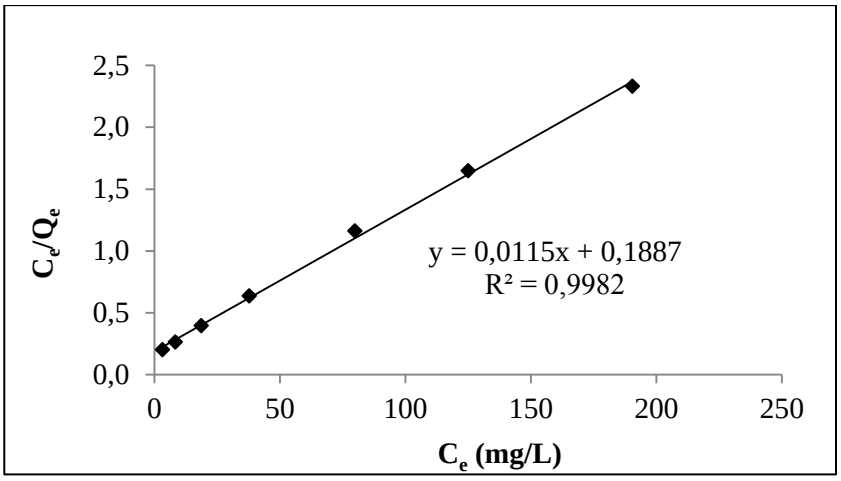


**Figure 3.54.** Linearized form of Langmuir isotherm for P(ClVBTA) at 45°C.

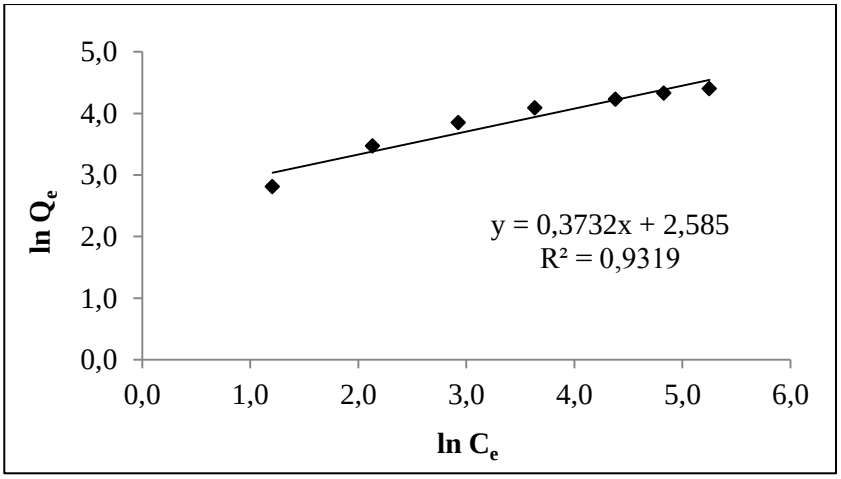


**Figure 3.55.** Linearized form of Freundlich isotherm for P(ClVBTA) at 45°C.

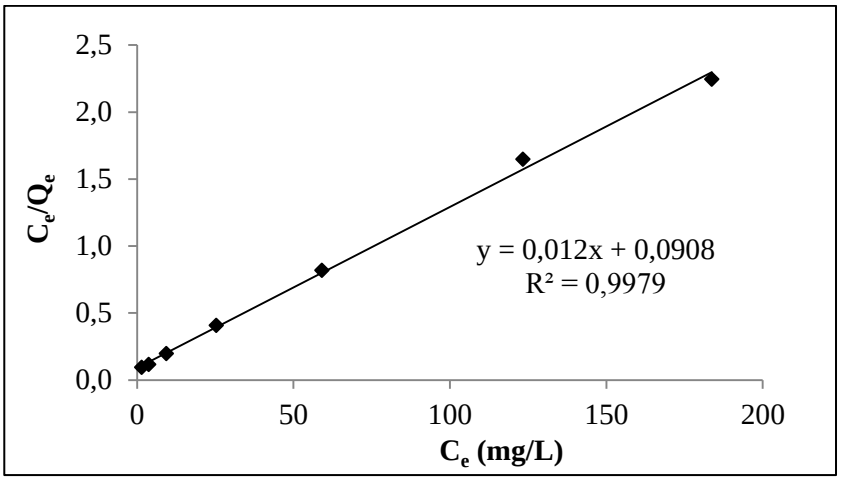


**Figure 3.56.** Linearized form of Langmuir isotherm for P(ClAPTA) at 25°C.

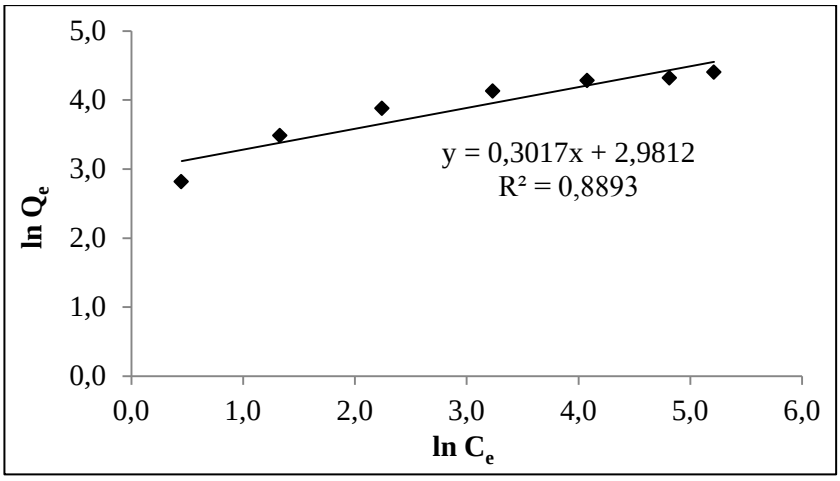


**Figure 3.57.** Linearized form of Freundlich isotherm for P(ClAPTA) at 25°C.

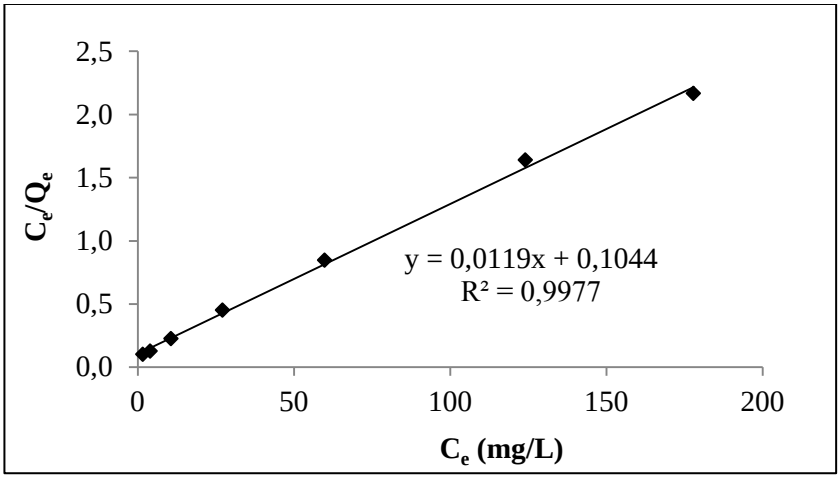


**Figure 3.58.** Linearized form of Langmuir isotherm for P(ClAPTA) at 35°C.

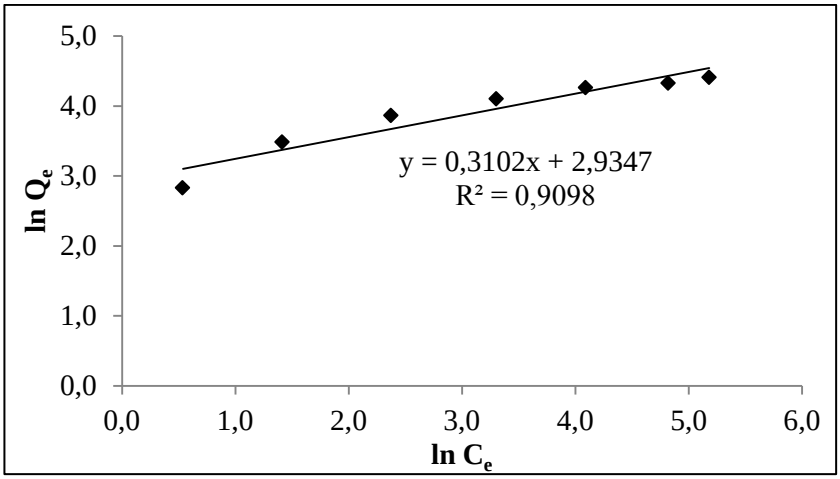


**Figure 3.59.** Linearized form of Freundlich isotherm for P(ClAPTA) at 35°C.

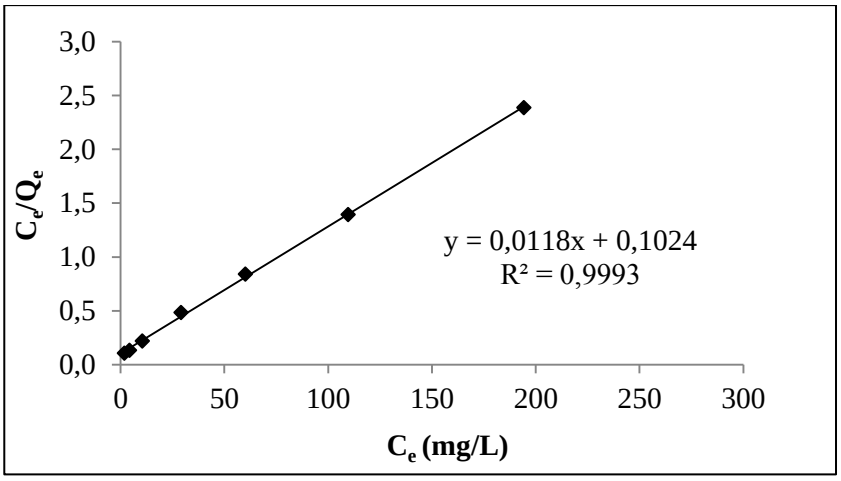


**Figure 3.60.** Linearized form of Langmuir isotherm for P(ClAPTA) at 45°C.

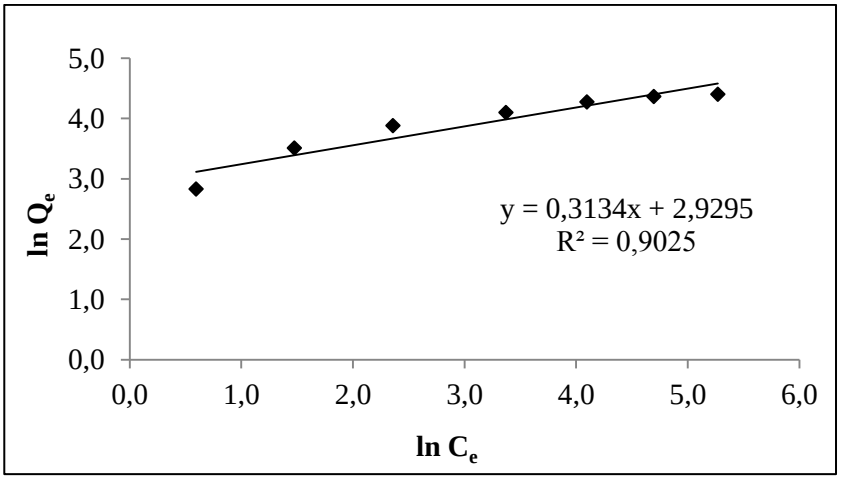


**Figure 3.61.** Linearized form of Freundlich isotherm for P(ClAPTA) at 45°C.

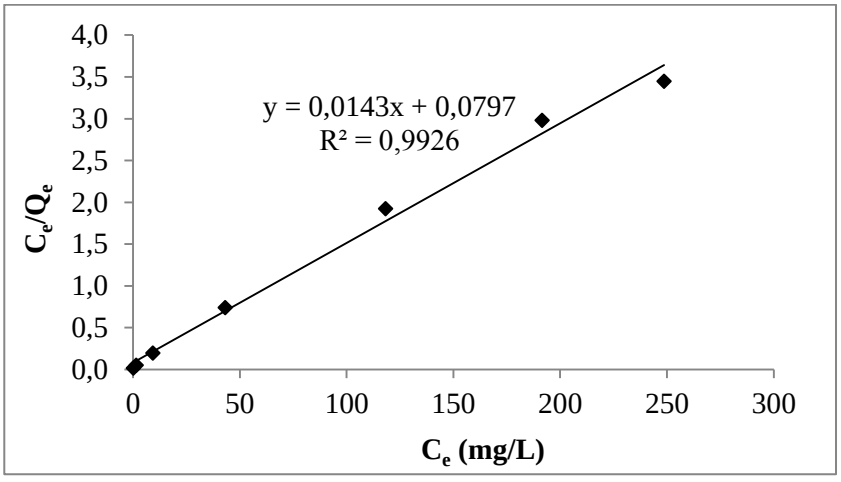


**Figure 3.62.** Linearized form of Langmuir isotherm for Amberlite IRA-400 at 25°C.

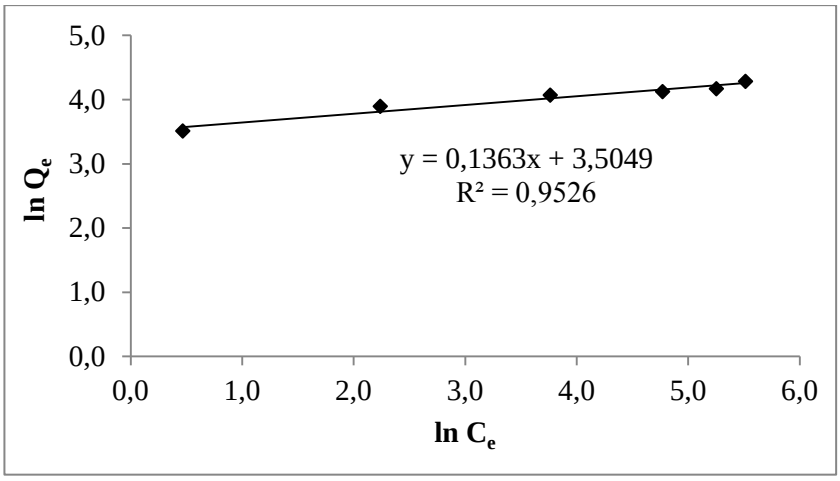


**Figure 3.63.** Linearized form of Freundlich isotherm for Amberlite IRA-400 at 25°C.

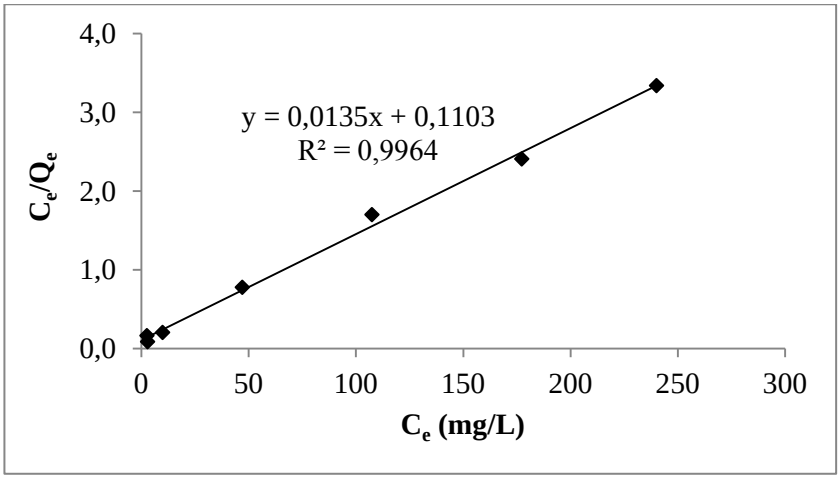


**Figure 3.64.** Linearized form of Langmuir isotherm for Amberlite IRA-400 at 35°C.

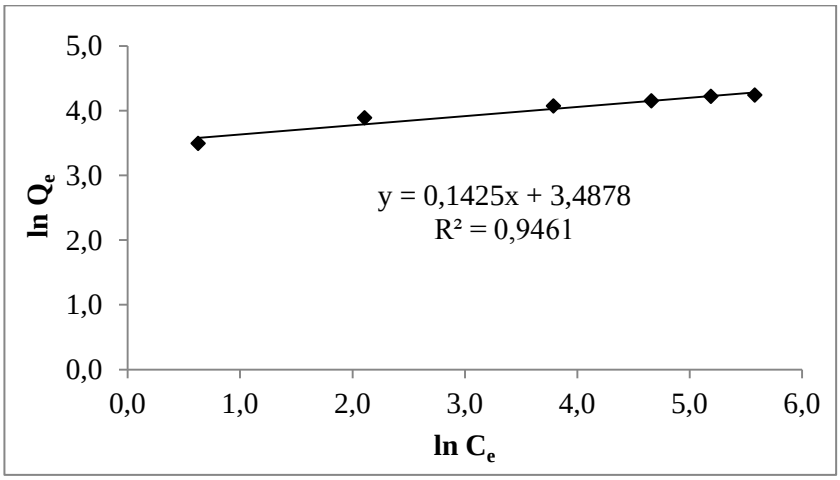


**Figure 3.65.** Linearized form of Freundlich isotherm for Amberlite IRA-400 at 35°C.

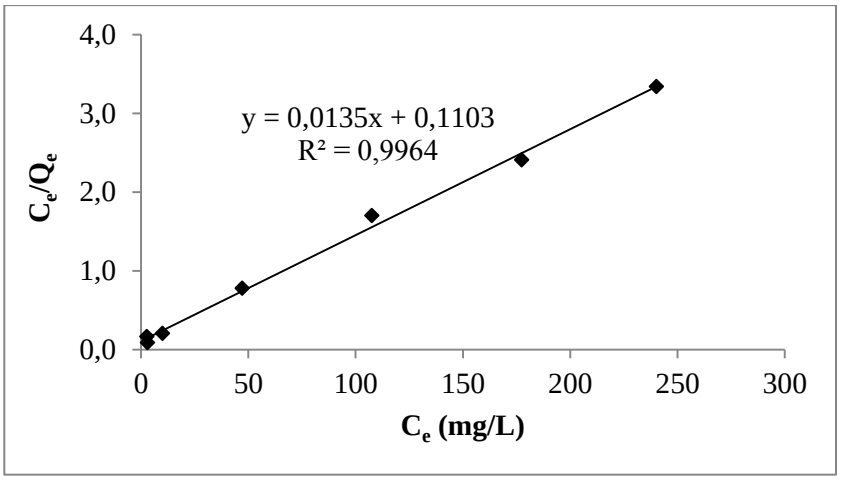


**Figure 3.66.** Linearized form of Langmuir isotherm for Amberlite IRA-400 at 45°C.

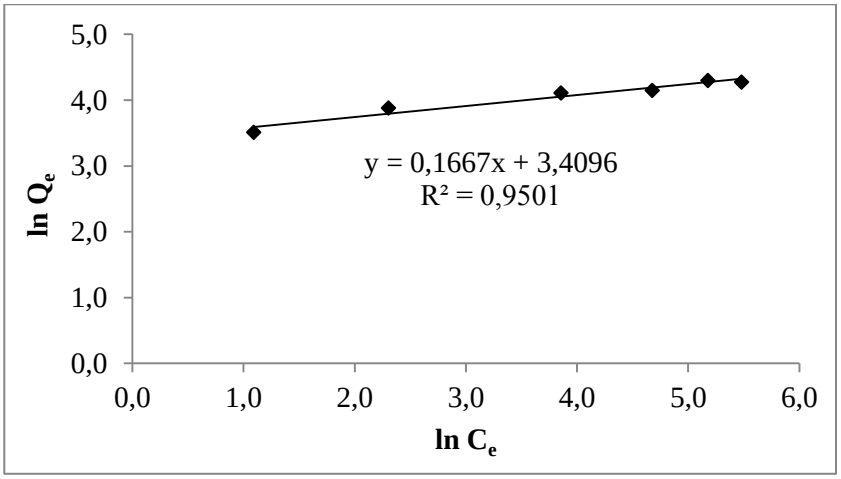


**Figure 3.67.** Linearized form of Freundlich isotherm for Amberlite IRA-400 at 45°C.

**Table 3.6.** Evaluation of equilibrium data obtained for P(ClVBTA), P(ClAPTA) and Amberlite IRA-400.

| Resin | Temperature (°C) | $R^2$ | |
|---|---|---|---|
| | | Langmuir Isotherm | Freundlich Isotherm |
| P(ClVBTA) | 25 | **0.9995** | 0.8964 |
| | 35 | **0.9977** | 0.8906 |
| | 45 | **0.9982** | 0.9319 |
| P(ClAPTA) | 25 | **0.9979** | 0.8893 |
| | 35 | **0.9977** | 0.9098 |
| | 45 | **0.9993** | 0.9020 |
| Amberlite IRA-400 | 25 | **0.9926** | 0.9526 |
| | 35 | **0.9987** | 0.9461 |
| | 45 | **0.9964** | 0.9501 |

### 3.3.4 Kinetic tests

The kinetic behaviors of P(ClVBTA), P(ClAPTA) and Amberlite IRA-400 for Cr(VI) removal were investigated with batch-mode sorption tests.

Figure 3.68 illustrates the relative concentration decrease of Cr(VI) versus time for each resin. The removal of Cr(VI) using P(ClVBTA) increased with time and reached the equilibrium in 3 min with a 97% of Cr(VI) removal, in 3 min with a 98% of Cr(VI) removal with P(ClAPTA), in 3 min with a 60% of Cr(VI) removal with Amberlite IRA-400 .

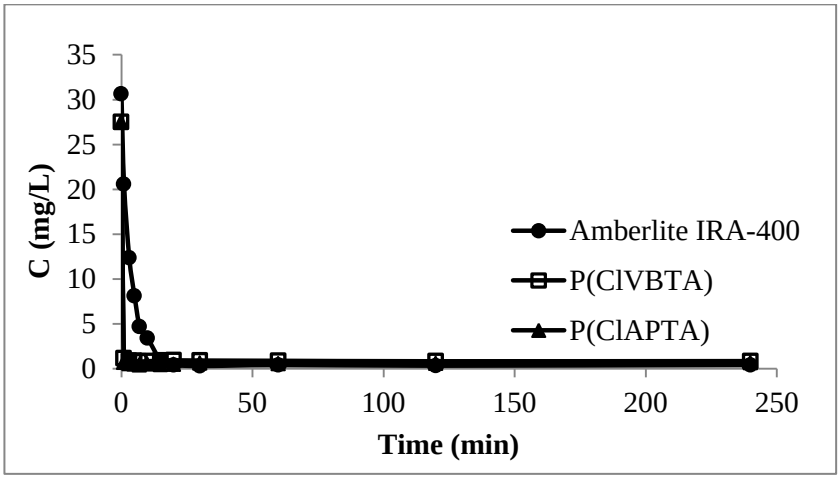


**Figure 3.68.** Effect of resin type on Cr(VI) sorption kinetics using Amberlite IRA-400, P(ClVBTA) and P(ClAPTA).

#### 3.3.4.1 Mathematical modeling

The kinetic data obtained for the resins P(ClVBTA), P(ClAPTA) and Amberlite IRA-400 were evaluated with pseudo-first-order and pseudo-second-order kinetics models using Eqs. 3.4 and 3.7 that were given in Section 3.3.1. The graphs of log(qe-qt) versus t and t/qt versus t were plotted for first-order and second-order kinetic models, respectively (Figures 3.69-3.74).

The correlation coefficients ($R^2$) of pseudo-second-order kinetics are greater than those of pseudo first-order-kinetics those of for P(ClVBTA), P(ClAPTA) and Amberlite IRA-400. The correlation coefficients were given in Table 3.7.

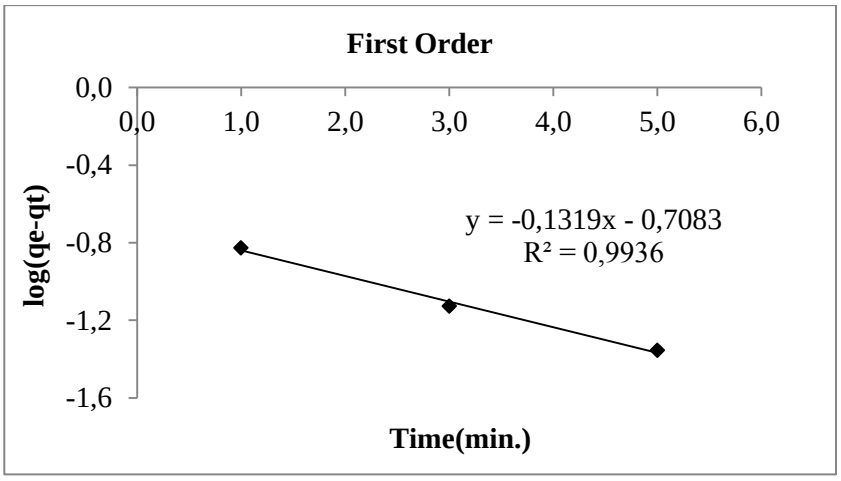


**Figure 3.69.** Evaluation of kinetic data using pseudo-first-order kinetic model for P(ClVBTA).

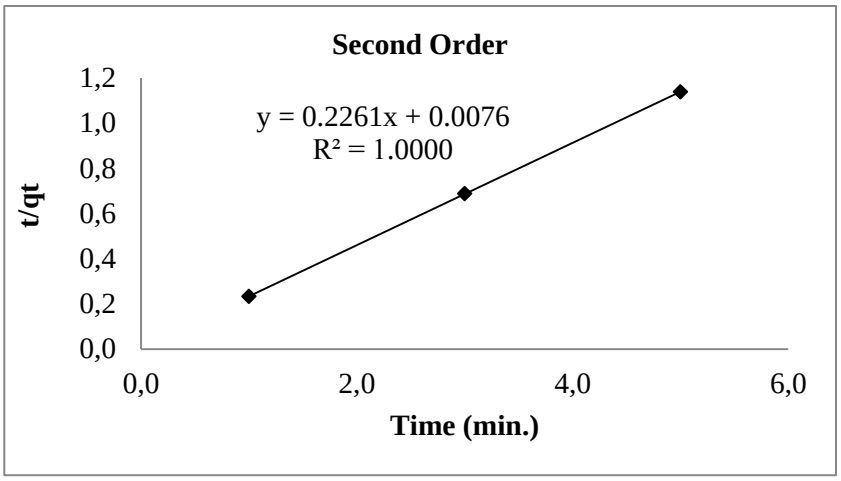


**Figure 3.70.** Evaluation of kinetic data using pseudo-second-order kinetic model for P(ClVBTA).

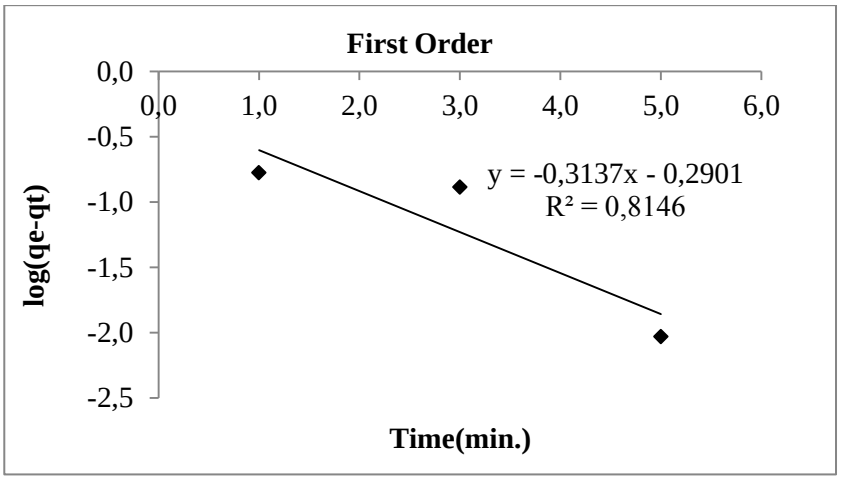


**Figure 3.71.** Evaluation of kinetic data using pseudo-first-order kinetic model for P(ClAPTA).

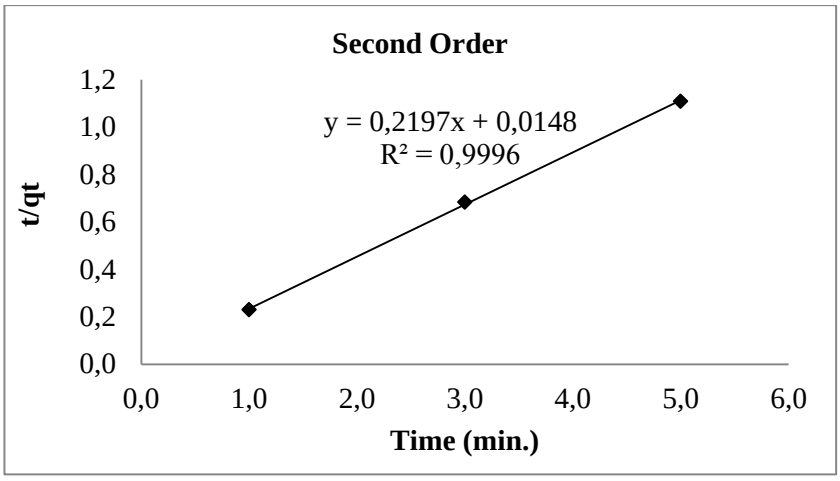


**Figure 3.72.** Evaluation of kinetic data using pseudo-second-order kinetic model for P(ClAPTA).

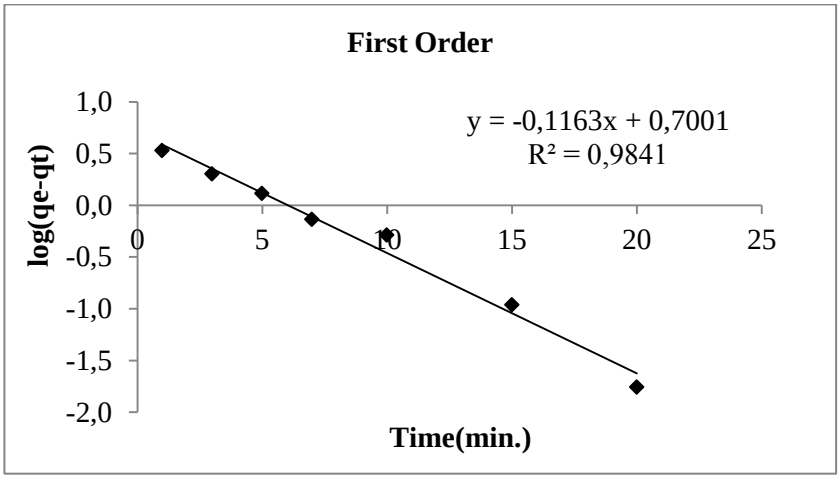


**Figure 3.73.** Evaluation of kinetic data using pseudo-first-order kinetic model for Amberlite IRA-400.

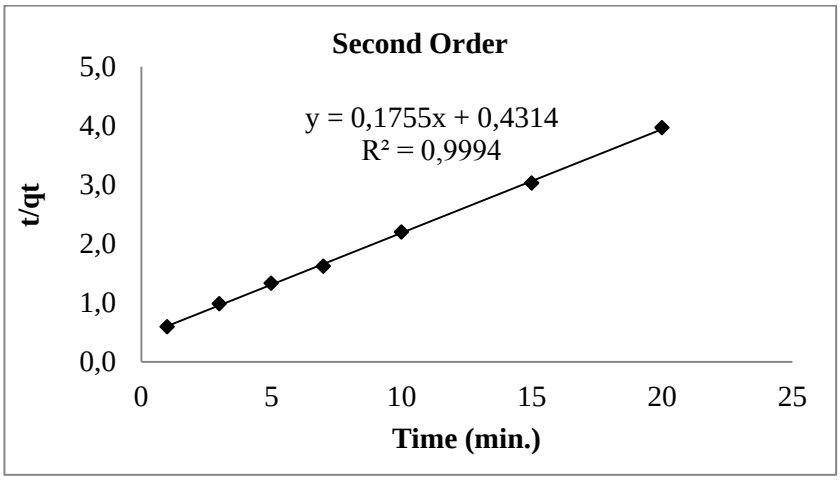


**Figure 3.74.** Evaluation of kinetic data using pseudo-second-order kinetic model for Amberlite IRA-400.

**Table 3.7.** Evaluation of sorption kinetic data obtained using conventional kinetic modeling for P(ClVBTA), P(ClAPTA) and Amberlite IRA-400.

| Resin | $R^2$ | |
|---|---|---|
| | **Pseudo-first-order** | **Pseudo-second-order** |
| P(ClVBTA) | 0.9936 | **1.0000** |
| P(ClAPTA) | 0.8146 | **0.9996** |
| Amberlite IRA-400 | 0.9841 | **0.9994** |

The kinetic data obtained were also evaluated with diffusional and reaction models for P(ClVBTA), P(ClAPTA) and Amberlite IRA-400 (Figures 3.75–3.80) as explained in Section 3.3.1.

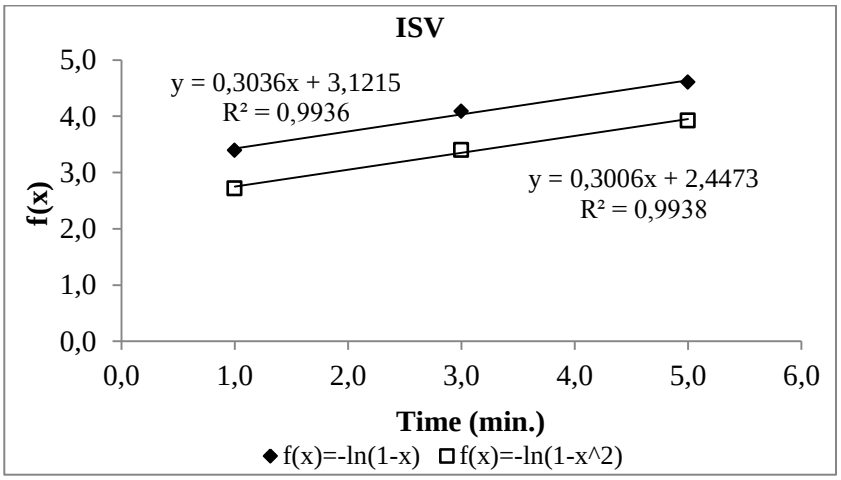


**Figure 3.75.** Evaluation of kinetic data using infinite solution volume model (ISV) for P(ClVBTA).

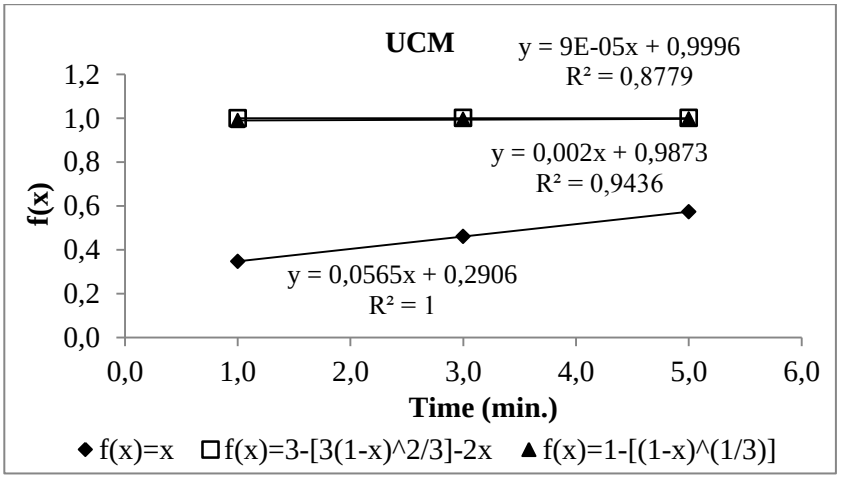


**Figure 3.76.** Evaluation of kinetic data using unreacted core model (UCM) for P(ClVBTA).

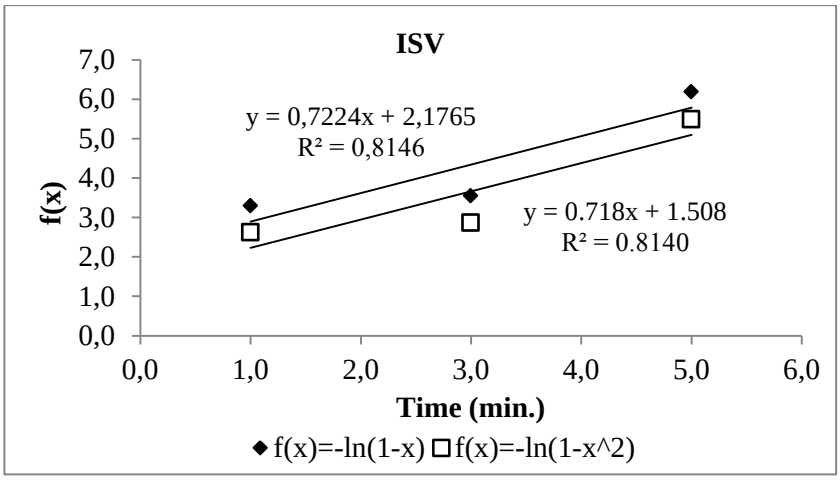


**Figure 3.77.** Evaluation of kinetic data using infinite solution volume model (ISV) for P(ClAPTA).

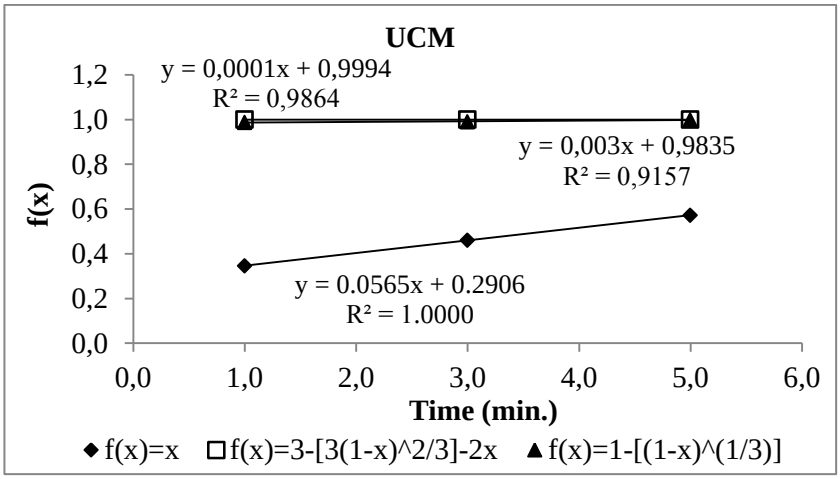


**Figure 3.78.** Evaluation of kinetic data using unreacted core model (UCM) for P(ClAPTA).

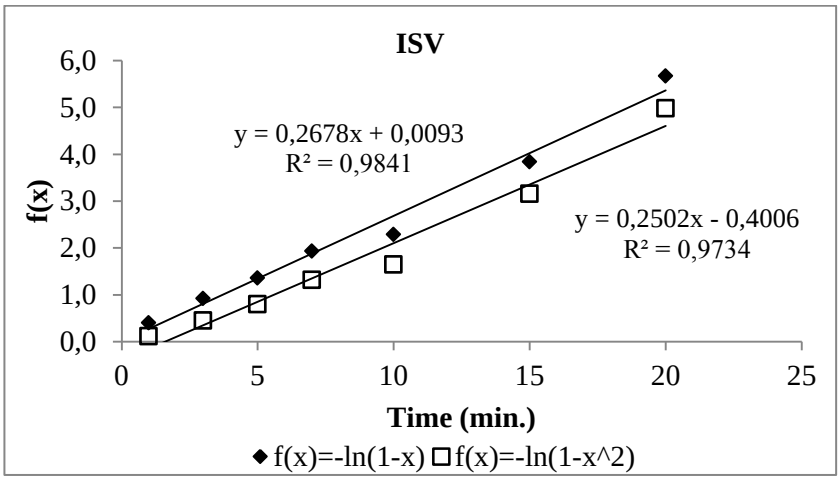


**Figure 3.79.** Evaluation of kinetic data using infinite solution volume model (ISV) for Amberlite IRA-400.

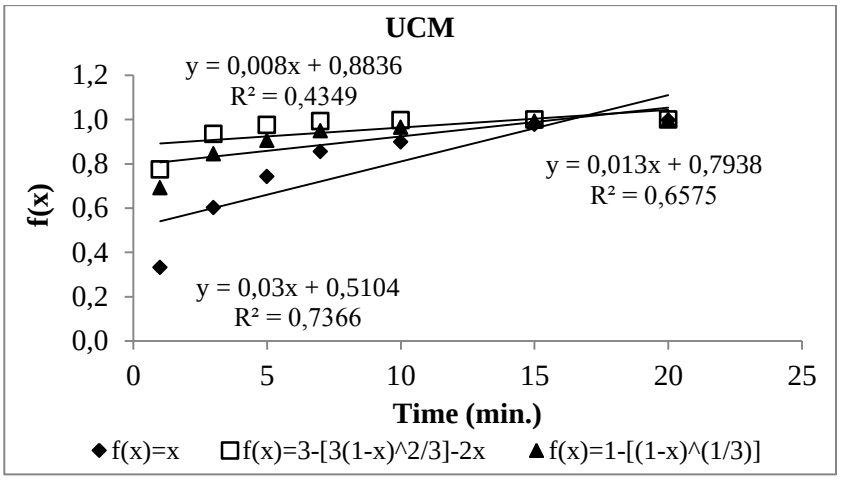


**Figure 3.80.** Evaluation of kinetic data using unreacted core model (UCM) for Amberlite IRA-400.

Table 3.8 shows the linear correlation coefficients obtained from the plots of f(X) function versus time as shown in Figures 3.75–3.80.

**Table 3.8.** Evaluation of sorption kinetic data obtained using diffusional and reaction models for P(ClVBTA), P(ClAPTA) and Amberlite IRA-400.

| RESIN | $R^2$ | | | | |
|---|---|---|---|---|---|
| | ISV | | UCM | | |
| | Film diffusion $-\ln(1-X)$ | Particle diffusion $-\ln(1-X^2)$ | Liquid film $X$ | Reacted layer $3-3(1-X)^{2/3}-2X$ | Chemical reaction $1-(1-X)^{1/3}$ |
| P(ClVBTA) | **0.9936** | **0.9938** | **1.0000** | 0.8779 | 0.9436 |
| P(ClAPTA) | **0.8146** | 0.8140 | **1.0000** | 0.9864 | 0.9157 |
| Amberlite IRA-400 | **0.9841** | 0.9734 | **0.7366** | 0.4349 | 0.6575 |

According to the obtained results the rate determining step was film diffusion for each resins.

### 3.3.5 Selectivity studies

In order to evaluate the selectivity of P(ClAPTA), P(ClVBTA), and Amberlite IRA-400 resins for Cr(VI), the sorption tests were carried out in the presence of $SO_4^{2-}$ and $Cl^-$ co-existing anions at 500 mg/L of concentration. Figures 3.81-3.83 show that in the presence of $Cl^-$ and $SO_4^{2-}$ ions, sorption capacities of ion exchange resins for Cr(VI) removal were not influenced significantly.

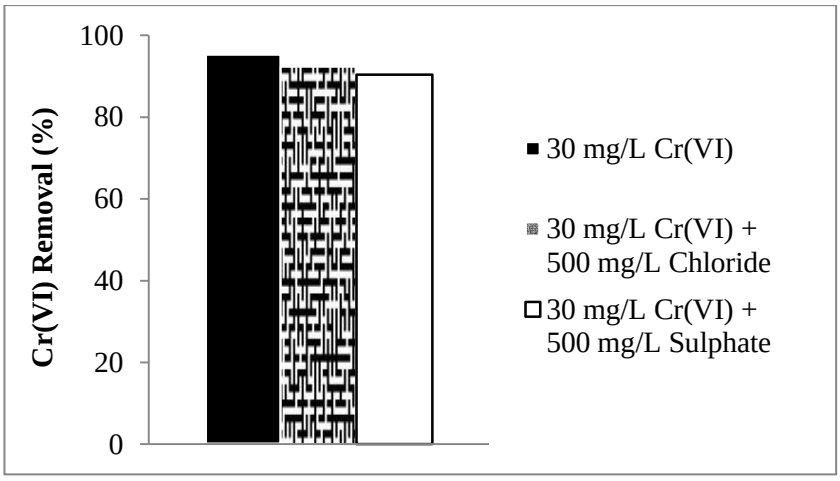


**Figure 3.81.** Cr(VI) removal in the presence of 500 mg/L chloride and sulphate anions by P(ClVBTA).

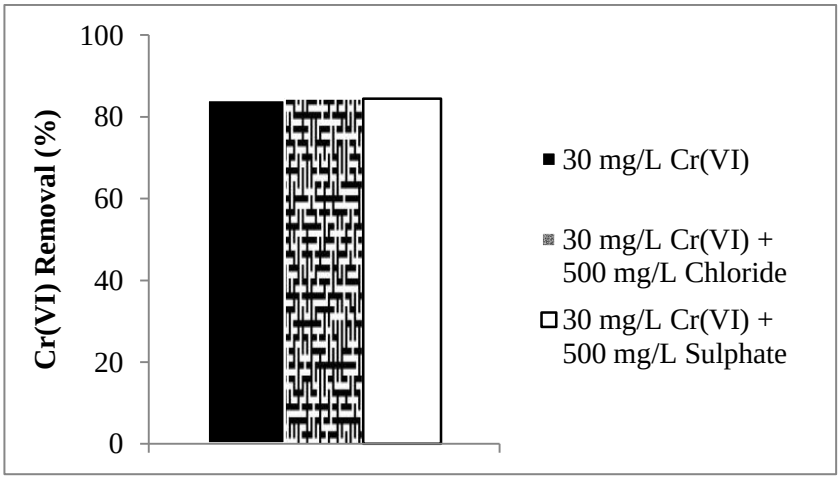


**Figure 3.82.** Cr(VI) removal presence of 500 mg/L chloride and sulphate anions by P(ClAPTA).

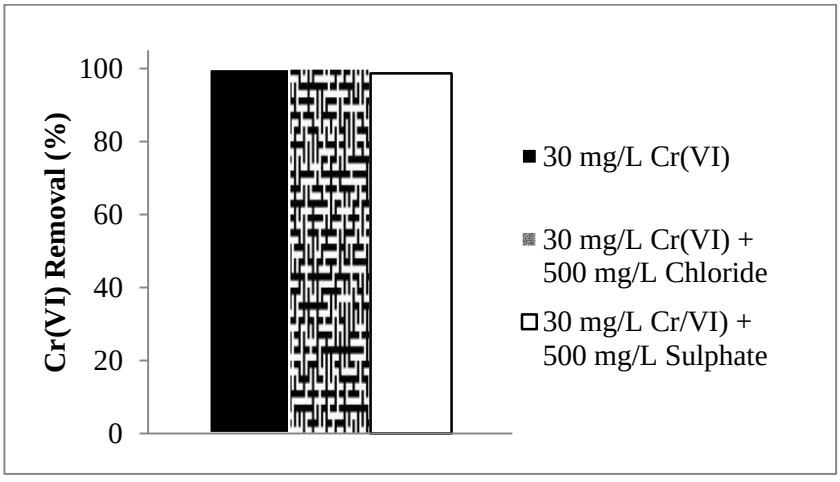


**Figure 3.83.** Cr(VI) removal presence of 500 mg/L chloride and sulphate anions by Amberlite IRA-400.

## 4. CONCLUSIONS

In this thesis, Cr(VI) removal from water was investigated by Aliquat 336 impregnated Diaion HP 20 and Diaion HP 2MG. Removal studies were performed using batch and column studies.

According to study of the effect of SIR amount on Cr(VI) removal from aqueous solutions, removal percentage of Cr(VI) increased with the increase in SIR amount. Obtained results showed that 1.00 g-SIR/50 mL solution was found as the optimum SIR concentration for removal of Cr(VI) with 97%, 88%, 92% of efficiency using HP 20 based SIRs in the impregnation ratio of 1 g Aliquat 336/g-resin, 2 g Aliquat 336/g-resin and 3 g Aliquat 336/g-resin, respectively. 1.00 g-SIR/50 mL solution was also found as the optimum SIR concentration for removal of Cr(VI) with 98%, 91%, 93% of efficiency using Cr(VI) using HP 2MG based SIRs in the impregnation ratio of 1 g Aliquat 336/g-resin, 2 g Aliquat 336/g-resin and 3 g Aliquat 336/g-resin, respectively.

Equilibrium data were obtained for Cr(VI) sorption onto HP 20 and HP 2MG based SIRs. The experimental data for HP 20 and HP 2MG based SIRs prepared at the impregnation ratio of 1 g Aliquat 336 / g-resin fit well to Langmuir model whereas the sorption data of SIRs with the impregnation ratios of 2 g Aliquat 336 / g-resin and 3 g Aliquat 336 / g-resin fits well to Freundlich model.

In kinetic tests, the removal of Cr(VI) using HP 20 based SIR increased with time and reached the equilibrium in 120 min with a 85% Cr(VI) removal at the impregnation ratio of 1 g Aliquat 336/g-resin, in 30 min with a 99% Cr(VI) removal at the impregnation ratio of 2 g Aliquat 336/g-resin, in 30 min with a 90% Cr(VI) removal at the impregnation ratio of 3g Aliquat 336/g-resin. The removal of Cr(VI) using HP 2MG based SIR increased with time and reached the equilibrium in 180 min with a 95% Cr(VI) removal at the impregnation ratio of 1 g Aliquat 336/g-resin, in 60 min with a 99% Cr(VI) removal at the impregnation ratio of 2 g Aliquat 336/g-resin, in 60 min with a 98% Cr(VI) removal at the impregnation ratio of 3 g Aliquat 336/g-resin.

The batch kinetic data obtained for Cr(VI) removal were evaluated by using conventional kinetic models. The correlation coefficients of pseudo-first-order kinetics ($R^2$) are greater than those of pseudo-second-order kinetics for HP 2MG

based SIR prepared at the impregnation ratio of 1 g Aliquat 336/g-resin and HP 20 based SIR prepared at the impregnation ratio of 2 g Aliquat 336/g-resin. However, pseudo-second-order kinetic model was better for other impregnation ratios of HP 20 and HP 2MG based SIRs.

The kinetic data obtained were also evaluated with diffusional and reaction models for HP 20 and HP 2MG based SIRs. The maximum correlation coefficients for the linear models show that the rate is particle diffusion controlled according to ISV models for HP 20 based SIR at the impregnation ratios 1 g Aliquat 336/g-resin and 2 g Aliquat 336/g-resin, although film diffusion controlled at the impregnation ratio of 3 g Aliquat 336/ g-resin. The rate is liquid film controlled according to UCM models for HP 20 based SIRs at the impregnation ratios of 1 g Aliquat 336/g-resin, 2 g Aliquat 336/g-resin and 3g Aliquat 336/ g-resin. For HP 2MG based SIRs at the impregnation ratios of 1 g Aliquat 336/g-resin, 2 g Aliquat 336/g-resin and 3 g Aliquat 336/ g-resin the rate is particle diffusion controlled mostly according to ISV models. The rate is liquid film controlled according to UCM models for HP 2MG based SIRs at the impregnation ratios of 1 g Aliquat 336/g-resin, 2 g Aliquat 336/g-resin and 3 g Aliquat 336/ g-resin.

In column-mode tests performed, HP 20 and HP 2MG based SIRs prepared at the impregnation ratios of 1 g Aliquat 336/g-resin, 2 g Aliquat 336/g-resin and 3 g Aliquat 336/g-resin were used. According to the breakthrough capacities, calculated by accepting the breakthrough point as 1.0 mg Cr(VI)/L, the highest breakthrough capacity was obtained with the SIRs prepared at impregnation ratio of 3 g Aliquat 336/g-resin for both polymer matrix. When HP 20 and HP 2MG polymer matrix were compared, the total and breakthrough capacities of HP 20 based SIRs were higher than those of HP 2MG based SIRs.

The removal of Cr(VI) from aqueous solution was also investigated by ion exchange resins P(ClAPTA) and P(ClVBTA) that were synthesized in University of Concepcion and the commercial resin Amberlite IRA-400.

Effect of pH on the Cr(VI) removal from aqueous solution was investigated for P(ClAPTA), P(ClVBTA) and Amberlite IRA-400. The results show that Cr(VI) sorption by these resins depends on pH. The highest removal of Cr(VI) was observed at pH 6-10 for each resin.

Equilibrium data were obtained for Cr(VI) sorption onto P(ClAPTA), P(ClVBTA) and Amberlite IRA-400. Effect of temperature to sorption of Cr(VI) onto P(ClAPTA), P(ClVBTA) and Amberlite IRA-400 was investigated. It was found that increase of temperature does not effect Cr(VI) sorption. In addition, the equilibrium data were evaluated using Langmuir and Freundlich adsorption isotherm models. The experimental data for these resins fit well to Langmuir model for each temperature.

The batch kinetic data obtained for Cr(VI) removal was evaluated by using conventional kinetic models. The correlation coefficients of pseudo-second-order kinetics ($R^2$) are greater than those of pseudo-first-order kinetics for P(ClVBTA), P(ClAPTA) and Amberlite IRA-400.

The kinetic data obtained were also evaluated with diffusional and reactional models for P(ClVBTA), P(ClAPTA) and Amberlite IRA-400. According to the obtained results, the rate determining step was film diffusion for each resin.

Cr(VI) removal was performed in the presence of 500 mg/L of $SO_4^{2-}$ and 500 mg/L of $Cl^-$ anions using P(ClVBTA), P(ClAPTA) and Amberlite IRA-400. The results show that the presence of the co-existing ions did not influence the removal of Cr(VI). With P(ClVBTA), 90%, 92% and 95% of Cr(VI) removals were obtained, in the presence of 500 mg/L of $SO_4^{2-}$, 500 mg/L of $Cl^-$ and without any co-existing ions, respectively. Cr(VI) removal obtained was %84 with P(ClAPTA) in the presence of 500 mg/L of $SO_4^{2-}$ and %84 in the presence of 500 mg/L of $Cl^-$ and without co-existing ions. With Amberlite IRA-400, 99%, 100% and 100% of Cr(VI) removals were obtained, in the presence of 500 mg/L of $SO_4^{2-}$, 500 mg/L of $Cl^-$ and without any counter ions, respectively.

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**Presentations in National Conferences**

1. Ö. Kuşku, M.Arda, Ü.Yüksel, N.Kabay, M.Yüksel, Çözücü emdirilmiş reçinelerle sulu çözeltilerden Cr(VI) iyonunun uzaklaştırılması, VI. Ulusal Analitik Kimya Kongresi, September 3-7, 2012, Hatay (poster presentation)

2. Ö. Kuşku, M. Arda, P. Santander, E.Altıok, N. Kabay, M. Yüksel, Ü. Yüksel, Nano gözenekli polimer adsorbanlardan hazırlanmış Aliquat 336 emdirilmiş reçinelerin Cr(VI) gideriminde kolon performanslarının incelenmesi, 1. Ege Nanoteknoloji Günleri, 18-19 Nisan 2013, Ege Üniversitesi, İzmir, Türkiye (poster presentation)

**SCI Papers Submitted**

B. Rivas, Ö. Kuşku, B. Urbano, M. Arda, N. Kabay, M. Bryjak, 'A comparative study for removal of Cr(VI) by ion exchange resins bearing quaternary ammonium groups', submitted to Journal of Chemical Technology and Biotechnology (2013).

**Projects Submitted During Undergraduate Education**

2209/A - Üniversite Öğrencileri Yurt İçi Araştırma Projeleri Destek Bursu – **(**Şelatlayıcı ve Kuvvetli Asidik Reçineler ile Ağır Metal İyonlarının ($Pb^{2+}$; $Cu^{2+}$ ve $Cd^{2+}$) Giderilmesi**)**

**Projects Involved During Graduate Education**

1. Project Number: EÜ-2011-FEN-092, Çeşitli Polimerik Adsorbanlardan Çözücü Emdirilmiş Reçinelerin Hazırlanması ve Bu Reçinelerin Sulu Çözeltilerden Cr(VI) İyonlarının Gideriminde Kullanılması.

2. Innovative Materials and Methods for Water Treatment-CHILTURPOL2 (supported by FP7-People 2010 IRSES-Marie Curie Actions) (2011-2012) (Faculty of Chemistry, Concepcion University of Chile/ between March 20-June 15, 2012 financially supported for 3 months as a research staff through this project).

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