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## **Improvement of the Sorption Performance of Nanosilica and Polymeric Solid Supports by Impregnation with Ionic Liquid for the Removal of Cr(VI) Ions from Aqueous Solutions**

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**Abstract:** In this study, supported ionic liquid phase (SILP) adsorbents were prepared by immobilizing the ionic liquids (ILs) onto nanosilica and styrene-divinylbenzene copolymer (SDVB) particles for the removal of hexavalent chromium, Cr(VI) ions from aqueous solutions. Three types of ionic liquids such as tricapryl methyl ammonium nitrate [A336][NO<sub>3</sub>], tricapryl methyl ammonium chloride (Aliquat® 336) and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIMTf<sub>2</sub>N) were successfully impregnated onto solid supports by following physical impregnation method through ultrasonication. The structural and morphological characterizations of the adsorbents were investigated by FTIR, SEM, and BET analysis. The thermal stabilities of the ionic liquid impregnated solid particles were also characterized by TGA analysis. Metal sorption performances of the prepared sorbents were investigated by considering Cr(VI) ions' sorption regarding the thermodynamic and kinetic aspects. The effects of various analytical parameters on the sorption of Cr(VI) ions such as IL loading ratio, pH of the solution, adsorbent dosage, initial metal ion concentration were studied. Cr(VI) ions were quantitatively adsorbed in the pH range of 2-4 with the impregnation ratio of 1 g-IL/g-support by all type of adsorbents. Moreover, the removal percentages of chromium ions were found to be 99.53%, 99.50% and 100% for TT600-TS, MOX80-TS and XAD-A, respectively. Sorption isotherms were also fitted with Langmuir equation and they were exhibited favorable sorption behavior.

**Keywords:** Adsorption; ionic liquid; supported ionic liquid phase (SILP); chromium.

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## INTRODUCTION

In recent years, various methods have been extensively studied for the removal of heavy metal ions from wastewater. These technologies include chemical precipitation (1), ion-exchange (2), adsorption (3), membrane filtration (4), coagulation, flocculation, flotation, and electrochemical methods (5). Among all these methods, adsorption is considered as the effective technique for the removal of heavy metals from wastewater (6). Generally, there are several factors specifying the efficiency of the adsorption such as the surface area, pore size, and distribution as well as the surface chemistry of the adsorbents. Porous materials (e.g. silica, macroporous polymer beads) are employed as promising sorbents for heavy metal removal due to their good physicochemical properties such as porosity and high surface area. However, they do not lead satisfactory efficiency with respect to weak binding properties (7). Consequently, the modification of porous sorbents by immobilization or incorporation of the functional groups is particular concern to increase the surface adsorption and to enhance the removal efficiency. In many applications, ionic liquids (ILs) can be used as chelating agent due to their unique properties (8).

ILs are salts consisting completely of organic cations and inorganic or organic anions. Their better charge distribution and larger ion size compared to classical inorganic salts result in melting points below 100 °C. By variation of anions and cations, solubility, reactivity, and coordination properties of the ILs can be changed according to the special requirements of the given application (9). Their applications in separation processes are very promising because of their unique properties, such as negligible vapor pressure, good thermal stability, tunable viscosity and miscibility with water and organic solvents, and high ionic conductivity (10). In recent years, ILs have been immobilized onto silica or polymeric supports (known as supported ionic phases-SILPs) in order to combine the advantages of IL with those of porous solid supports (11). SILP technology is regarded as a fundamental and new approach to obtain liquid-containing solid materials that do not evaporate, made through surface modification of porous solid by dispersing a thin film of ILs onto it (9). SILP are resulting in materials of low toxicity, which are environmentally benign and have a wide range of separation applications. These materials are prepared by covalent attachment of an IL to a support surface or simply impregnation of the IL phase (12).

In recent years, several researchers have focused on the use of novel adsorbents impregnated with ionic liquids (3, 8-11). Al-Bishri *et al.* investigated the uptake of lead from the aqueous solution by imidazolium-based ionic liquid impregnated onto nano-silica

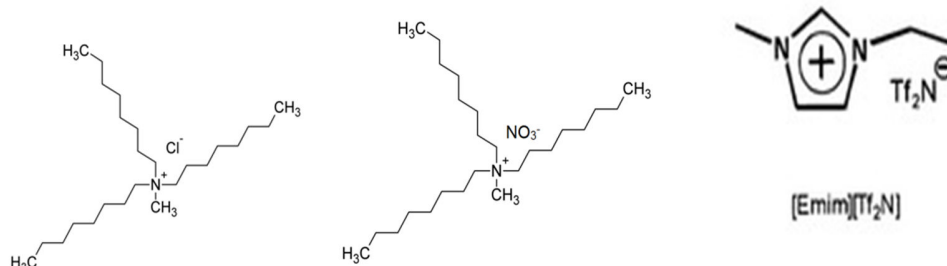
sorbents (13). Lupa *et al.* immobilized the aminophosphate-based ionic liquid onto the organic and inorganic supports in order to be used as adsorbents for the removal of thallium from aqueous solutions (14,15). Navarro *et al.* investigated the bismuth(III) recovery from hydrochloric acid solution using Amberlite XAD-7 impregnated with a tetraalkylphosphonium ionic liquid (16). The improvement of Cu (II) ion sorption performance of the nano-silica and nano-alumina particles by the immobilization of 1-ethyl-3-methyl imidazolium bis (trifluorosulfonyl) imide [Emim<sup>+</sup>Tf<sub>2</sub>N<sup>-</sup>] ionic liquid was investigated by Gizli and Arabacı (8).

In this study, the enhancement of Cr(VI) ion's sorption performance of the nanoparticles and polymeric supports were investigated by modifying them with three different types of ionic liquids. The diversity of support and ILs were selected of different porous properties and chemical structure among those commonly used in heavy metal removal processes. Modification was achieved via ultrasound-assisted physical impregnation method. Ultrasonification, as an unconventional method, is less time-consuming and ensures the effective distribution of IL onto solid supports (17). The physicochemical and morphological characteristics of the prepared adsorbents were investigated by Fourier-Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), Brunauer–Emmett–Teller (BET) surface area analysis. On the other hand, thermal behaviors of the adsorbents were investigated by Thermal Gravimetric Analysis (TGA). Cr(VI) ion sorption performance of adsorbents have been examined by considering the effect of sorption conditions (pH of solution, initial concentration, adsorbent dose) and loading ratio of IL per unit mass of solid supports. Fixed bed column sorption studies were also carried out to obtain the breakthrough performances of SILPs.

## MATERIAL AND METHOD

### Chemicals

In this study, three types of ionic liquids such as tricapryl methyl ammonium chloride [A336][Cl] known as Aliquat® 336, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [EMIMTf<sub>2</sub>N] and tricapryl methyl ammonium nitrate [A336][NO<sub>3</sub>] were used. Although [A336][Cl] and EMIMTf<sub>2</sub>N was obtained from Sigma Aldrich, [A336][NO<sub>3</sub>] was synthesized. Chemical structures of ionic liquids are shown in Figure 1.



**Figure 1** Chemical structures of ionic liquids.

a) Aliquat® 336 (left), b) [A336][NO<sub>3</sub>] (middle), c) [EMIM][Tf<sub>2</sub>N] (right).

The stock solution of Cr(VI) (1000 mg/ L) was prepared by dissolving an appropriate amount of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in deionized water. The working solutions of different concentrations were prepared by diluting the stock solution. The K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> salt was supplied from Merck, Germany.

Nano-silica (Aerosil TT600 and Aerosil MOX 80) particles from Evonic Industries and polymeric particles (Amberlite XAD-16) from Fluka, were used as supporting materials. Properties of polymeric and nanoparticles are given in Table 1 and Table 2, respectively.

**Table 1.** Properties of polymeric support (Amberlite XAD-16).

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

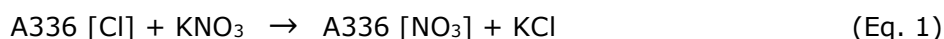
**Table 2.** Properties of nanoparticles.

Properties	Commercial Name	
	Aerosil TT600	AerosilMOX80
Particle Size [nm]	40	30
Surface Area[m <sup>2</sup> /g]	200	80
pH	3.5-4.5	3.5-4.5
Content	SiO <sub>2</sub> (%100)	SiO <sub>2</sub> (%99)/Al <sub>2</sub> O <sub>3</sub> (%1)

## EXPERIMENTAL PROCEDURE

### Task-Specific Ionic Liquid Synthesis

Task-specific ionic liquid, A336 [NO<sub>3</sub>] was prepared by anion metathesis reaction as shown in the following equation.



To achieve the reaction, commercial Aliquat® 336 ionic liquid and 2 M of KNO<sub>3</sub> solutions were contacted for 1 hour during vigorous stirring. The phases were then separated by using a separating funnel followed by washing with distilled water. These steps were repeated for 4 times. Completion of the reaction was controlled by checking the Cl<sup>-</sup> ion content of the ionic liquid by using AgNO<sub>3</sub> indicator.

### Preparation of the Ionic Liquid Impregnated Adsorbents

SILP adsorbents were prepared by the impregnation of the ionic liquid onto polymeric- and silica-based nanoparticle supports through ultrasound-assisted physical impregnation method (18). The solid supports were immersed into 25 mL of ethanol to swell in the solvent media. Then, a proper amount of ionic liquid was added and sonicated at a frequency rate of 35 Hertz during 60 minutes. The particles were then left to dry at ambient conditions. The IL content of adsorbents were varied between 0.1 ~ 2.0 g-IL/g-solid support and the prepared SILPs are abbreviated as given in the Table 3.

**Table 3.** Abbreviation of prepared SILPs.

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

### Characterization of Adsorbents

The chemical structures of prepared SILPs were investigated by a Fourier Transform Infrared Spectrometer (FTIR), (Perkin Elmer Spectrum 100) within the wavenumber range of 650-4000 cm<sup>-1</sup> to identify the functional groups both before and after the modification of the

support materials with IL. The surface morphologies of adsorbents were analyzed by using Scanning Electron Microscopy (SEM), (Philips XL 30S FEG) operating at an accelerating voltage of 2.00 kV. The particles were coated with a gold layer in order to make them conductive. Surface areas and pore volumes of silica adsorbents were investigated by Brunauer–Emmett–Teller (BET) analysis (Micromeritics Gemini V model). Thermal Gravimetric Analysis (TGA) was carried out using Perkin Elmer Diamond TG/DT model to investigate thermal behavior of the support materials before and after modification with IL.

### Adsorption Studies

**Batch Sorption Studies:** Adsorption studies were carried out by contacting 10 mL of Cr(VI) (50 mg/L) solution with 0.2 g SILP at 25°C during 24 h. Chromium ion concentrations were measured by Atomic Absorption Spectrophotometer (AAS) (Varian 10+) before and after adsorption studies.

The uptake of Cr(VI) by the adsorbent was calculated from the following equation,

$$q_e = \frac{(C_0 - C_e) * V}{W} \quad (\text{Eq. 2})$$

Where  $q_e$  is the uptake of Cr(VI) by SILP at equilibrium (mg/g),  $C_0$  and  $C_e$  are the initial and equilibrium Cr(VI) concentrations in the aqueous phase (mg/L),  $V$  is the volume of solution (mg/L), and  $W$  is the amount of adsorbent (g).

The sorption percentage of the nanoparticles was calculated as given in Equation (3),

$$\text{Sorption}(\%) = \frac{(C_0 - C_e)}{C_0} * 100 \quad (3)$$

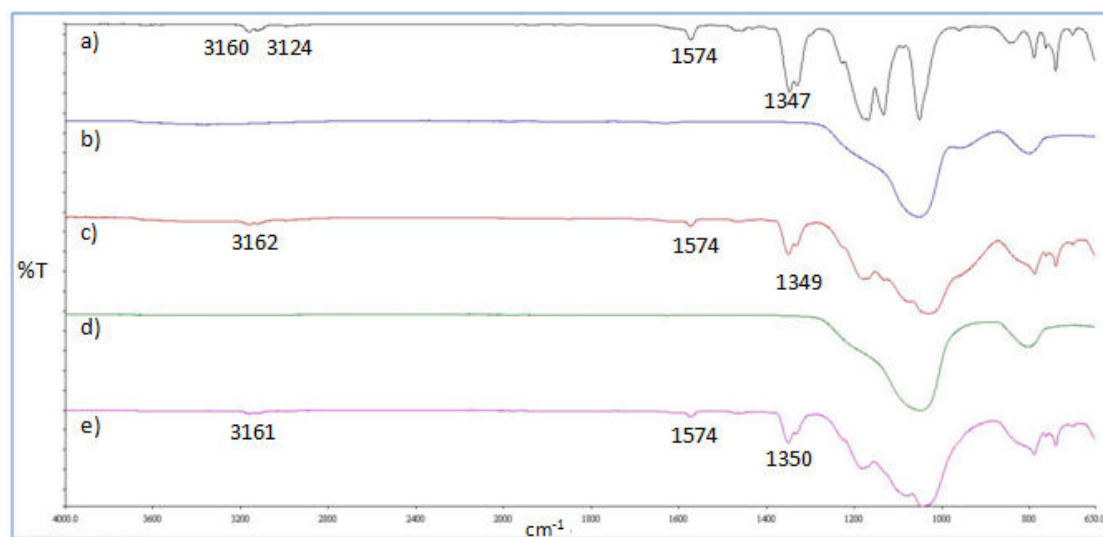
### Column Sorption Studies:

Column sorption studies were carried out by passing 0.01 M of Cr(VI) solution through a packed bed column having 0.7 cm inner diameter and filled with 1 mL of adsorbent. The flow rate of the solution has been fixed as 15 bed-volumes per hour (BV/h) by the help of peristaltic pump (Peristaltic PR-2003).

## RESULTS AND DISCUSSION

### Characterization of Adsorbents

The FTIR spectra of nanoparticles (TT600 and MOX80) before and after modification with EMIMTf<sub>2</sub>N ionic liquid are shown in Figure 2.

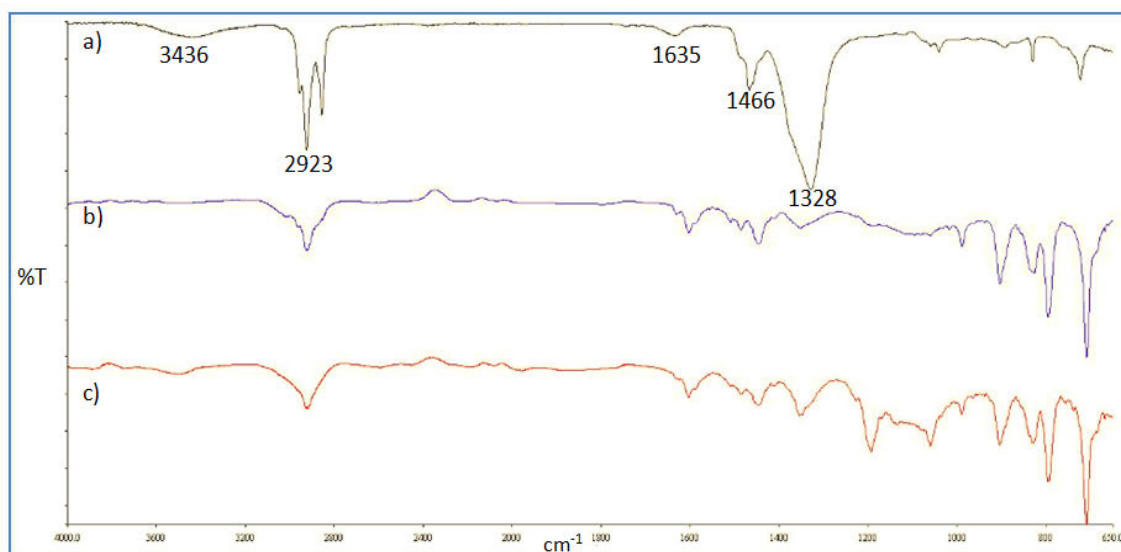


**Figure 2.** FTIR spectrum of nanoparticles prepared with [EMIMTf<sub>2</sub>N].

- a) EMIMTf<sub>2</sub>N ionic liquid b) TT600- before modification c) TT600-after modification  
d) MOX80-before modification e) MOX80- after modification.

The characteristic peaks of the EMIMTf<sub>2</sub>N ionic liquid are seen around 3160 cm<sup>-1</sup> and 1574 cm<sup>-1</sup> in Figure 2-a can be attributed to the C-H and C=C vibrations of the imidazole ring of ionic liquid. In addition, the infrared region of the ionic liquid spectrum between 1400 cm<sup>-1</sup> and 1000 cm<sup>-1</sup> is mainly dominated and characterized by several peak assignments that are related to the anionic moiety (19). In all spectra of the silica nanoparticles (Figure 2 b,c,d,e), the bands around 1090 cm<sup>-1</sup> assigning the stretching vibrations of the Si-O-Si groups of the silica backbone are observed. It can also be seen in all the spectra of modified nanoparticles that two new absorption peaks at the position of 3161 cm<sup>-1</sup> and 1574 cm<sup>-1</sup> appeared after nanoparticles are treated with IL. These adsorption peaks confirm the modification of nanoparticles with ionic liquid.

The FTIR spectrum of SDVB particles (XAD-16) before and after modification with [A336][NO<sub>3</sub>] ionic liquid is shown in Figure 3.



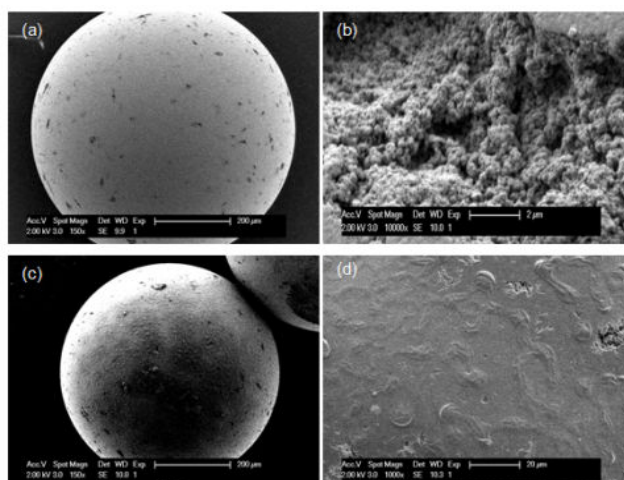
**Figure 3.** FTIR of p-SILP prepared with [A336][NO<sub>3</sub>] a) ionic liquid [A336][NO<sub>3</sub>]. b) XAD-16- before modification c) XAD-TS after modification.

In the spectra of [A336][NO<sub>3</sub>] (Figure 3.a), the peaks around the position of 2923 cm<sup>-1</sup> can be attributed to the characteristic absorption of -CH<sub>3</sub> of alkyl chain and at the position of 1466 and 1328 cm<sup>-1</sup> are based on the structure of quaternary ammonium moiety of the ionic liquid. The peak located at 1328 cm<sup>-1</sup> (Figure 3-c) is pronounced after modification of polymer particles with ionic liquid.

The morphological change of polymeric support by modification with A336 [NO<sub>3</sub>] can be quantified from SEM images presented in Figure 4.

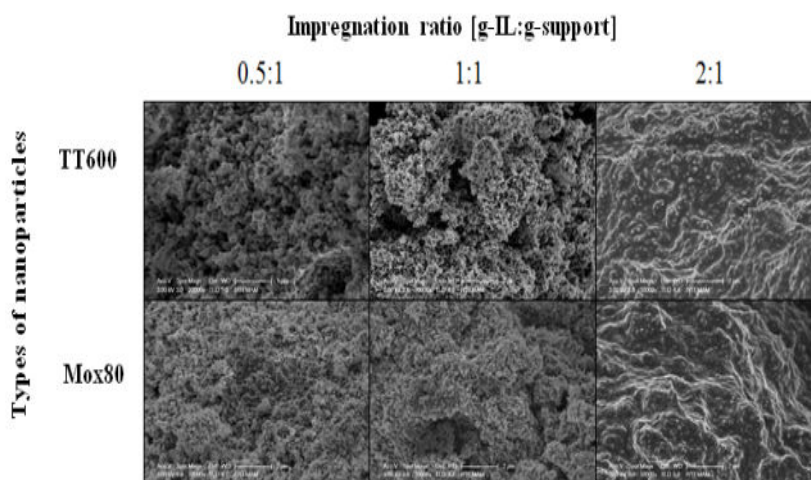
It is evident from Figure 4 that immobilization of the ionic liquid on the surface of polymeric particles lead to a characterized change on the morphology. It is clearly observed that porous structures of the particles are filled with ionic liquid.





**Figure 4.** SEM images of SILP adsorbent (loading ratio = 1:1 [g-IL: g-support]). a) Before impregnation (X150), b) Before impregnation (X10000), c) After impregnation (X150), d) After impregnation (X1000).

The change in surface morphology of nanoparticles by immobilization of IL at various ratios is shown in Figure 5.



**Figure 5.** SEM images of nanoparticles impregnated with ionic liquid at the loading rate of 0.5:1, 1:1, 2:1 (g-IL: g-support).

It is evident from Figure 5 that immobilization of IL on the surface of the nano-silica and nano-alumina particles resulted in a pronounced and characterized change on the surface morphology. It is clearly observed that ILs cover the surface of the nanoparticles which lead to a decrease in the surface area by modification.

The surface pore characteristics of the solid supports modified by various amount of ILs were examined by BET and surface area analyzer. BET results are given in Supplementary

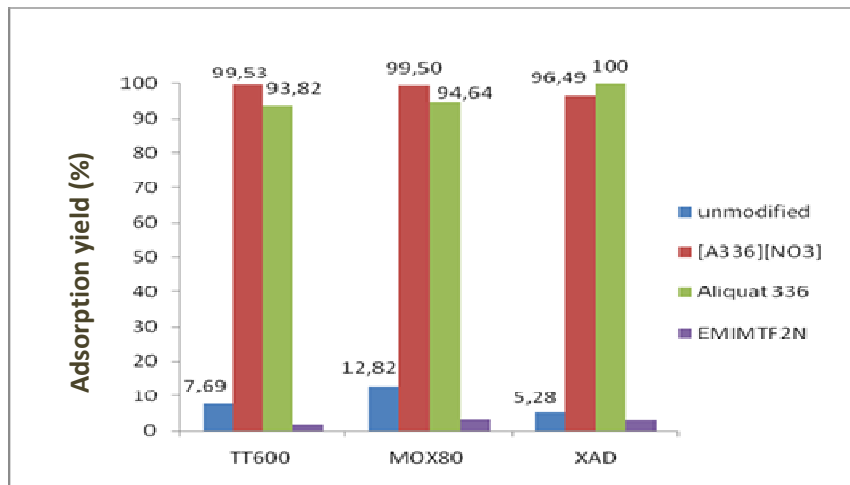
Documents, (Tables A1 and A2 and Figure A1). In BET analysis results, there are noticeable declines in the surface area ( $\text{m}^2/\text{g}$ ) pore volume ( $\text{cm}^3/\text{g}$ ) and pore size values after modification of the all type of solid supports with ionic liquid. Surface area of nanoparticles decreased from 200 ( $\text{m}^2/\text{g}$ ) to 9.3 ( $\text{m}^2/\text{g}$ ) for TT600 and from 80 ( $\text{m}^2/\text{g}$ ) to 19.7 ( $\text{m}^2/\text{g}$ ) for MOX80. All support materials follow the same trend as drastic decline in the surface area with increasing in the ionic liquid loading ratio. These can be concluded that ILs are filled into the pores of solid supports.

Thermal behaviors of the adsorbents were characterized by TGA analysis (given in the Supplementary Document). It is evident from Figure 2.A that  $[\text{Emim}^+\text{Tf}_2\text{N}^-]$  started to decompose at 350 °C and decomposed almost completely at 500 °C. The weight loss of the nanoparticle adsorbents prepared at the impregnation ratio of 1:1 (g-IL/g-support) were below 3% at the temperature range of 20-350 °C. However, the nanoparticle supports started to decompose at moderately low temperatures (around 30 °C) and the mass loss of all types of nanoparticles were around 15% at the temperature range of 20-600 °C. SDVB polymeric type solid support also started to decompose at the temperatures below 100 °C but decomposition temperature of such type of supports were elevated to 200 °C by modification with ionic liquids. It can be concluded that the immobilization of ionic liquids may lead to improvement in the thermal stability of nano-silica and SDVB polymeric particles at the temperature range of 20-300 °C.

### **Cr(VI) Adsorption Experiments**

**Batch Sorption Studies:** A series of batch sorption tests were carried out to obtain the optimum sorption parameters such as adsorbent type, adsorbent dose, pH and concentration of adsorbate for the removal of Cr(VI) from aqueous solutions.

The results of the a comparative study for the sorption performance of prepared sorbents are shown in Figure 6.

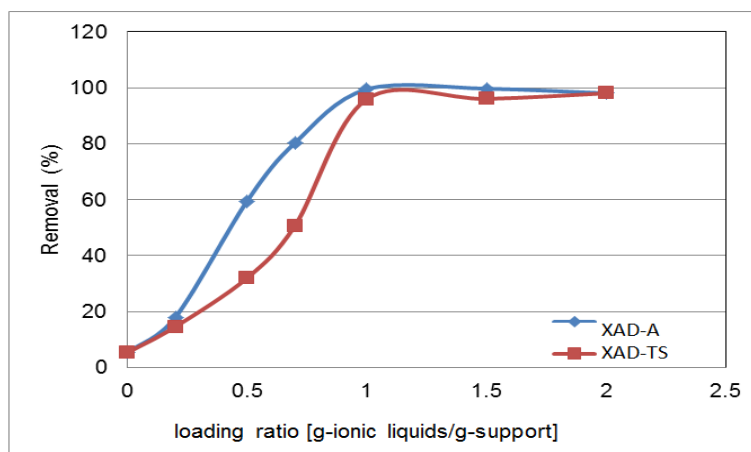


**Figure 6.** Adsorption performance of prepared adsorbents for Cr(VI) removal.

As seen in Figure 6, it is clearly observed that there is a significant increase in the adsorption percentage of all type of support materials after modification with Aliquat® 336 and A336[NO<sub>3</sub>] type ionic liquids. Adsorption yield of polymeric (XAD) adsorbent is increased from 5.28% to almost 100% after impregnation with Aliquat® 336 and A336[NO<sub>3</sub>]. Similar adsorption performances are also achieved by TT600 and MOX 80 nanoparticles. However, the sorption performances of all type of sorbents containing EMIMTf<sub>2</sub>N ionic liquid dramatically decreased comparing to the others. It can be concluded that Aliquat® 336 and A336[NO<sub>3</sub>] type ionic liquids might be attached to the solid support by electrostatic interactions and sorption takes place under the effect of anion exchange reaction. Since Cr(VI) occurs predominantly in the form of (HCrO<sub>4</sub>)<sup>-</sup> ions in aqueous phase at working pH value. On the other hand, EMIMTf<sub>2</sub>N ionic liquid does not play a role in an ion exchange reaction and repulsion effect is observed for that working pH range.

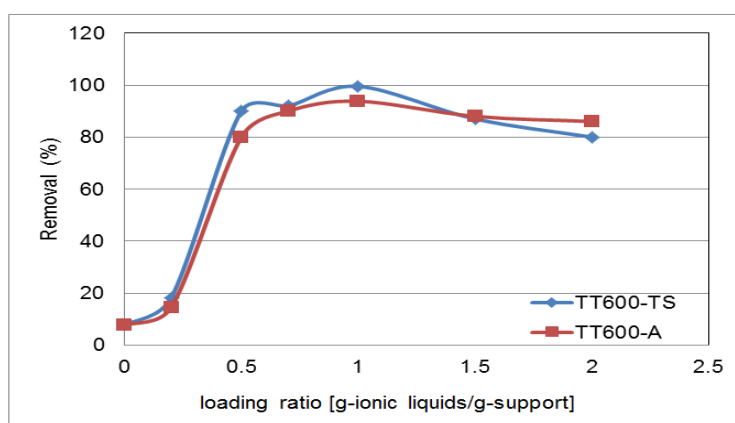
#### **Effect of IL Loading Ratio on the Sorption of Cr(VI) Ions**

The effect of the amount of ionic liquid loading ratio on the Cr(VI) adsorption percentages were investigated by using SILP containing various amount of IL(g) per solid support (g). The impregnation ratio was selected as 0.2:1, 0.5:1, 0.7:1, 1:1, 1.2:1, and 2:1 (g-IL/g-support). The effect of IL loading ratio on Cr(VI) removal performances for XAD, TT600, and MOX 80 are shown in Figure 7-9, respectively.

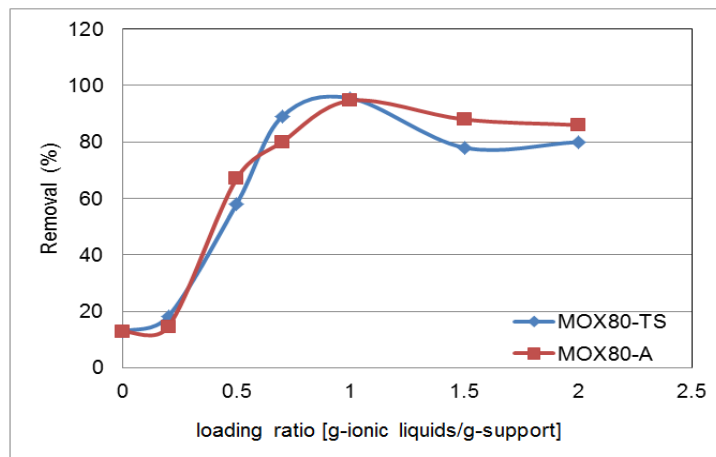


**Figure 7.** Effect of ionic liquid loading ratio on Cr(VI) removal performance of XAD supports.

At these conditions, it can be clearly seen from Figure 7 the increasing in the IL loading ratio of both XAD-A and XAD-TS increase the percentage of adsorption until the loading ratio of (1:1 g-IL/g-support and adsorption percentages are found nearly 100% and 96% for XAD-A and XAD-TS, respectively.



**Figure 8.** Effect of ionic liquid loading ratio on Cr(VI) removal performance of TT600.

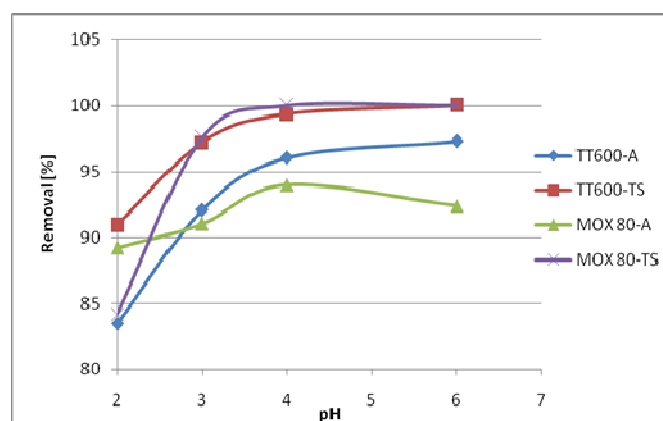


**Figure 9.** Effect of ionic liquid loading ratio on Cr(VI) removal performance of MOX 80.

In Figures 8 and 9, it is clearly seen that up to a certain value (1 g /g support) the adsorption yield of the ionic liquid increases with increasing loading ratios. After this value, it can be attributed that adsorption yield decreases with decreasing in the value of surface area because of the filling the pores of particle with IL for nanoparticles. Impregnation with A336[NO<sub>3</sub>] type ionic liquids demonstrated higher achievement compared to commercial ionic liquid for both MOX 80 and TT600. For further studies, IL loading ratio is chosen as 1:1 (g-IL/g-support) for all type of SILPs.

### Effect of Solution pH

The solution pH is one of the most important parameter to find out the adsorption capacity of adsorbents for Cr(VI) ions.

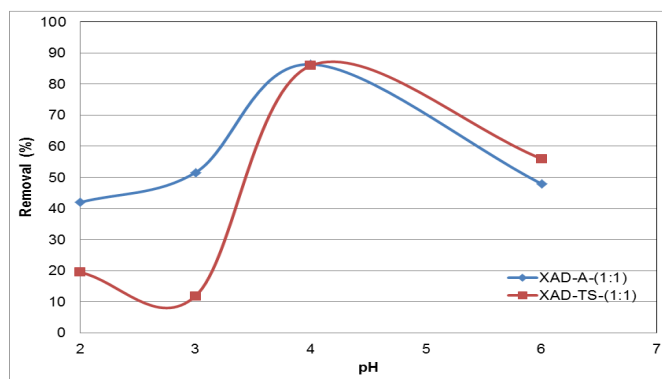


**Figure 10.** Effect of pH on the adsorption of Cr(VI) onto adsorbent (TT600 and MOX80).

In Figure 10, it is shown that the removal of Cr(VI) ion increases with increasing pH from 2 to 4. After the pH value of 4, nearly no further changes in percentage of adsorption yield is

observed. This situation can be explained by the predominant formation of  $\text{HCrO}_4^-$  ions reacted with anionic group of ionic liquid by ion exchange reactions in pH values between 2 and 4. Above pH 4 predominantly form of  $\text{CrO}_4^{2-}$  was formed in the solution.

The effects of pH on the adsorption of Cr(VI) onto SILP with polymeric support are shown in the Figure 11.



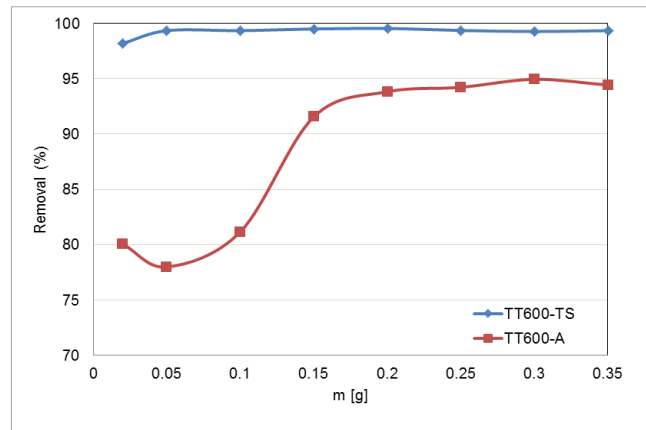
**Figure 11.** Effect of pH on the adsorption of Cr(VI) onto SILP adsorbent.

In Figure 11 it can be clearly seen that removal of Cr(VI) ions increases with increasing pH between 2 and 4. After pH 4, a sudden decrease is observed in the percentage removal. According to Figures 10 and 11, the optimal pH value is specified as 4.

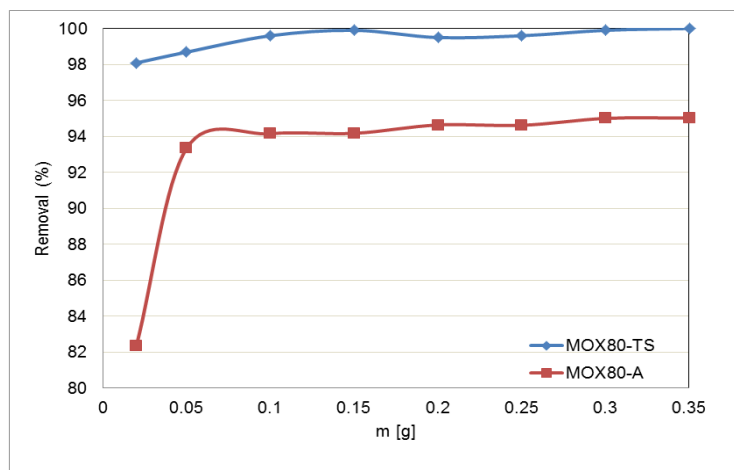
### Effect of Adsorbent Dose

The amount of sorbent significantly affects the extent of Cr(VI) sorption. Increase in sorbent dose leads to more surface areas which are available for adsorption resulting in an increase in the active sites on the sorbent. The effect of adsorbent dose (g) on the adsorption of Cr(VI) was studied in the range of 0.01~0.35 g adsorbent by contacting with 10 mL of solution at 30 °C during 24 hours. The initial concentration of Cr(VI) ion was set as 50 mg/L, and pH of the solution was adjusted to the value of 4.

The effects of adsorbent amount of nano particles (TT600 and MOX80) are shown in Figure 12 and 13.



**Figure 12.** Effect of adsorbent dose on the adsorption of Cr(VI) onto SILP (TT600).

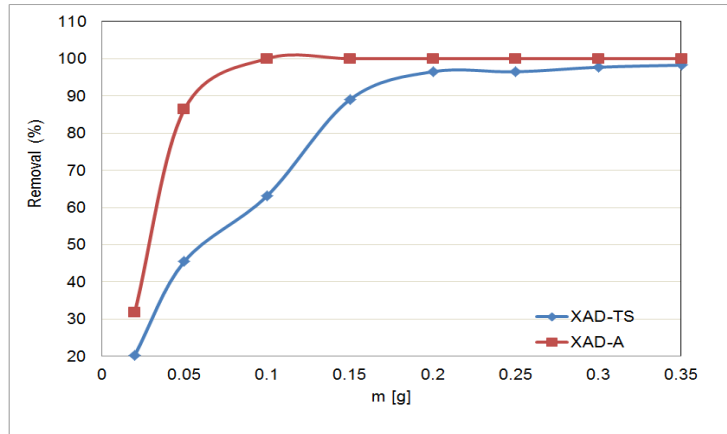


**Figure 13.** Effect of adsorbent dose on the adsorption of Cr(VI) onto SILP (MOX 80).

It is observed from Figure 12 and Figure 13 that the percentage removal of Cr(VI) ions reach to almost 100% for TT600-TS and MOX80-TS. Optimum adsorbent dose is determined as 0.1 g per 10 mL of Cr(VI) solution since the highest adsorption percentages is obtained at that condition.

TT600-TS and MOX 80-TS exhibited higher Cr(VI) sorption performance than that of TT600-A and MOX 80-A. The percentage removal of Cr(VI) ions increases from 82% to 94 %, with the increasing in the adsorbent amount of TT600-A from 0.1 to 0.2 g. Then, adsorption percentage value reaches a plateau with increasing amount of the adsorbent. Therefore, for TT600-A, the optimum adsorbent dose is selected as 0.2 g for the rest of the experimental studies. In Figure 13, similar trend can be observed for MOX80 with TT600. In

Figure 12, it can be explained that high adsorption efficiency is reached at around 0.1 g. Therefore, optimum adsorbent dose is determined as 0.1 g for MOX80-A. After this value it reaches to the plateau as seen in Figure 13.



**Figure 14.** Effect of sorbent dose on the adsorption of Cr(VI) onto SILP (XAD).

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

### Equilibrium Studies

The equilibrium adsorption isotherms are some of the most important data for determining the sorption performances of the modified particles through the potential affinity between the metal ion and the adsorbent, the bond energy, and the sorption capacity. The most commonly employed models, namely the Langmuir and Freundlich adsorption models, were used in this study in order to describe the relationship between the amount of Cr(VI) ion adsorbed per unit weight of the modified nanoparticles ( $q_e$ ) and the liquid-phase equilibrium concentration ( $C_e$ ) of the Cr(VI) ions. The linear forms of the Langmuir and Freundlich isotherms are represented by the following equations (4) and (5) respectively.

$$\frac{C_e}{q_e} = \frac{1}{q_{max}b} + \frac{C_e}{q_{max}} \quad (\text{Eq. 4})$$

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



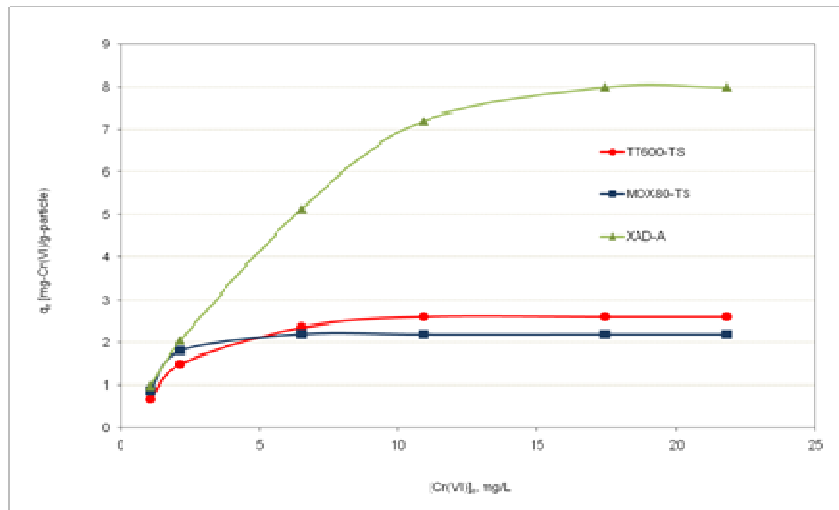
$$\log q_e = \log k_F + \frac{1}{n} \log C_e \quad (\text{Eq. 5})$$

Where  $k_F$  is a constant indicative of the adsorption capacity of the adsorbent (mg/g) and the constant  $1/n$  indicates the intensity of the adsorption.

The adsorption equilibrium data are conveniently represented by adsorption isotherms, which correspond to the relationship between the mass of the solute adsorbed per unit mass of adsorbent,  $q_e$  (mg/g), and the solute concentration for the solution at equilibrium,  $C_e$  (mg/L).

The preceding step, adsorption of Cr(VI) ions on the SILPs was studied according to Cr(VI) concentration range of 20-200 mg/L at optimum conditions. Equilibrium behaviors of TT600-TS, MOX80-TS and XAD-A are shown in Figure 15.

According to the values of correlation coefficient ( $R^2$ ) for Langmuir and Freundlich models, it can be seen that Langmuir model represents a good fit with the experimental data for all adsorbents. The Langmuir and Freundlich adsorption isotherm constants along with the correlation coefficients are given in Table 4.



**Figure 15.** Equilibrium behavior of SILPs.

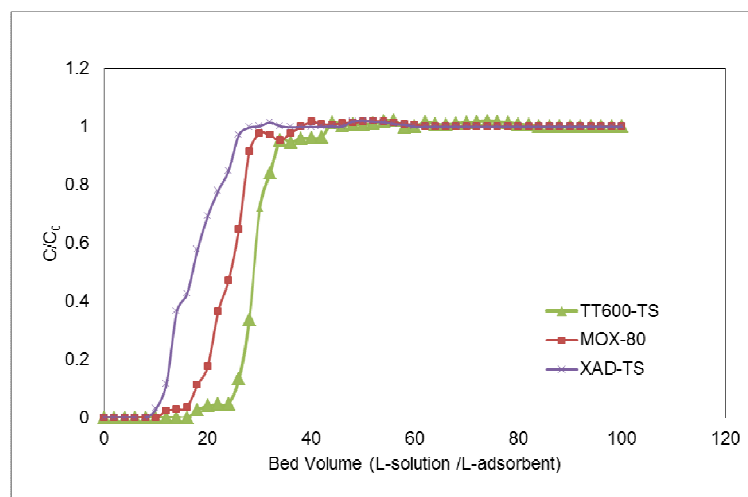
**Table 4.**Langmuir and Freundlich constants for the sorption of Cr(VI) on to SILPs.

MODEL	Constants	TT600-TS	MOX80-TS	XAD-A
Langmuir	$q_{max}$ (mg/g)	2.6137	2.2452	8.2508
	b	3.0929	7.5109	0.9106
	R <sup>2</sup>	0.9986	0.9992	0.9963
Freundlich	k (mg/g)	1.5628	1.6562	3.0068
	n	0.2883	0.1835	0.4982
	R <sup>2</sup>	0.7768	0.6303	0.9283

Maximum adsorption capacities ( $q_{max}$ ) for TT600-TS, MOX80-TS and XAD are found to be 2.61, 2.25 and 8.25 mg/g, respectively.

### Column Sorption Study

Continuous studies were carried out in a packed bed column of 0.7 cm inner diameter and breakthrough curves are shown in Figure 16 in this regard.

**Figure 16.** Breakthrough Curve.

When the breakthrough point is considered as the concentration of 5 mg/L; TT600-TS, MOX80-TS and XAD-A exhibited 15, 11 and 8 bed-volumes (L-solution /L-adsorbent) breakthrough capacities.

### CONCLUSION

In this study, supported ionic liquid phase (SILP) adsorbents were prepared by modification of nanosilica and SDVB polymeric particles with commercial and task-specific ionic liquids in order to enhance the Cr(VI) sorption capacities. The FTIR, SEM, and BET surface area analysis applied to the adsorbents proved the fact that the nanosilica and SDVB polymeric

supports were impregnated with the studied ionic liquids and also put in evidence in morphological changes.

Optimal conditions for the removal of Cr(VI) ions from aqueous solutions were determined by series of batch sorption studies. The sorption performance of prepared adsorbents was directly affected by the amount of IL confined (mL-IL: g-nanoparticle). The impregnation of the supports at a ratio of 1:1 showed higher sorption percentages up to 90%. Further increasing in the impregnation ratio led to decrease in Cr(VI) ion removal percentage. Optimal pH value was found to be 4 for all types of prepared adsorbents.

Adsorption isotherm data were well fit with Langmuir model representing favorable behavior with maximum sorption capacities up to 2.6, 2.2 and 8.2 mg Cr(VI)/g-SILP for TT600-TS, MOX80-TS, XAD-A, respectively. The column mode sorption performances of silica and SDVB particles were achieved for Cr(VI) removal and 5 mg/L was considered as the breakthrough point.

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

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### Türkçe Öz ve Anahtar Kelimeler

#### Nanosilika ve Polimerik Destek Malzemelerin Sulu Ortamlardan Cr(VI) İyonlarını Uzaklaştırma Performanslarının İyonik Sıvı Emdirilerek Geliştirilmesi

Nilay Gizli, Merve Arabacı

**Öz:** Bu çalışmada, sulu ortamlardan hegzavalent krom, Cr(VI) iyonlarının uzaklaştırılması için destekli iyonik sıvı faz (SILP) tutucular, iyonik sıvıların nanosilika ve polimerik destek malzemelere tutuklanması ile hazırlanmıştır. Trikapril metil amonyum nitrat [A336][NO<sub>3</sub>], trikapril metil amonyum klorür (Aliquat® 336) ve 1-etil-3-metilimidazolyum bis(triflorometilsülfonil)imid (EMIMTf<sub>2</sub>N) olmak üzere üç çeşit iyonik sıvı, ultrases varlığında fiziksel emdirme yöntemi izlenerek katı destek malzemelere başarı ile emdirilmiştir. Hazırlanan tutucuların modifikasyon öncesi ve sonrası kimyasal ve morfolojik yapıları, FTIR, SEM ve BET analizleri ile incelenmiştir. Ayrıca, iyonik sıvı emdirilmiş katı taneciklerin ısı davranışlarındaki değişim, TGA analizleri ile tanımlanmıştır. Hazırlanan tutucuların Cr(VI) iyonlarını tutma başarımları ise termodinamik ve kinetik davranışları temelinde incelenmiştir. İyonik sıvı yükleme oranı, çözelti pH'ı, tutucu miktarı, metal iyon derişiminin başlangıç değeri gibi analitik değişkenlerin tutucuların adsorplama verimi üzerine etkileri incelenmiştir. Hazırlanan tüm tutucu türleri için çözelti pH'ının 2-4 aralığında ve emdirme oranının 1 g-iyonik sıvı/g-destek malzeme olduğu koşullarda Cr(VI) iyonlarının dikkate değer bir biçimde uzaklaştırıldığı gözlemlenmiştir. Bununla birlikte, TT600-TS, MOX80-TS ve XAD-A tutucuları için krom iyonu uzaklaştırma yüzdeleri sırasıyla 99.53%, 99.50% ve 100%, olarak bulunmuştur. Ayrıca tutucuların denge davranışlarının Langmuir Denge İzotermlerine uyduğu sonucuna ulaşılmıştır.

**Anahtar kelimeler:** Adsorpsiyon, iyonik sıvı, destekli iyonik sıvı faz sistemleri, krom.

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