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Preparation and characterization of the sol-gel silica containing ionic liquids as a potential adsorbent for the removal of chromium (vi) ions from aqueous solutions

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Abstract

In this study ionic liquid mediated sol-gel silica adsorbents were prepared and characterized in order to investigate the sorption performances for the removal of Cr (VI) ions from aqueous solutions. High extracting ability of ILs was combined with the surface properties of silica substances by confining ILs in porous matrices. Commercial (Aliquat 336® and EMIMTf$_2$N) and synthesized ([A336][NO$_3$]) ionic liquids were incorporated directly by sol-gel process. Silica based adsorbents were being initiated with silica precursor (TEOS), water, alcohol and ionic liquid hydrolysis in the presence of an acid catalyst then completed with a condensation reaction. Chemical and morphological characterizations of prepared adsorbents have been investigated by FTIR, SEM and BET analysis. The materials exhibited average pore diameter of 2 nm, pore volume of 0.3 cm^3/g and BET surface area of 300–600 m^2/g. The sorption behaviors of adsorbents have been investigated by using a series of batch sorption studies. Cr(VI) sorption percentages of the adsorbents were enhanced by containing ILs up to 99% with the adsorption capacity of 31.74 mg/g. It can be concluded that sorption of Cr(VI) ions from aqueous solution by sol-gel silica based adsorbents containing Aliquat 336 takes place favorably and these type of adsorbents are promising agents in the adsorption processes.

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1. Introduction

Chromium has a wide range of industrial application area such as; metal plating, leather tanning, pigment and coating industries [1]. Chromium in aqueous solutions exists in a range of oxidation state from -2 to +6. Cr(VI) exhibits toxic effects for living organisms, therefore the allowable limit is kept at low concentrations. World Health Organization (WHO) has set this limit as 0.05 mg/L for the drinking waters [2]. For that reason it is very important to develop a process for selective removal of Cr(VI) ions from aqueous solutions.

Removal and extraction of dissolved heavy metal ions from aqueous media are generally accomplished by several methods including chemical precipitation, ion exchange, adsorption [3-6], membrane filtration [7], coagulation, flocculation, flotation, and electrochemical methods [8-10]. Among all these methods, adsorption is considered as the effective technique for the removal of heavy metals from aqueous solution because of advantages like the low cost, availability, profitability, ease of operation and efficiency [11, 12]. In general, the efficiency of the adsorption depends on many factors, including the surface area, pore size and distribution of it, as well as the surface chemistry of the adsorbents. The sorbents with a high specific surface area as a result of the porous character are generally needed for high adsorption efficiency [13].

Ionic liquids (ILs) are organic salts which have liquid form at room temperature. Because of this, they are recognized as Room Temperature Ionic Liquids (RTILs). The large number of possible ILs structures and their unique properties such as high thermal stability, non-flammability, negligible vapor pressure make them feasible to consider them as an opportunity to contribute to greenness in the various field [14]. In addition, ILs have adjustable hydrophobicity, polarity and selectivity compared with organic solvents when used for extraction [13, 15]. ILs can be used as metal extraction reagent for separation of metal ions [16, 17]. There are many advantages of ILs in separation processes such as high separation efficiency and high selectivity. However,

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some drawbacks of ILs are found in some liquid-liquid separation processes, such as large amount used, high viscosity leading unfavorably to dissolve and diffuse, difficulties of separation and recovery, and the low interface area [18]. To overcome these shortcomings, ILs can be incorporated onto highly porous solid supports in many different ways, such as simple impregnation, grafting, polymerization, sol–gel method and encapsulation [19]. Among these, sol-gel method has an incredible attention because of the advantages such as; (i) easy and inexpensive; (ii) functional groups are readily anchored on the substrate; and (iii) it can be used for the deposition of substrates that have complex surfaces or large surface areas [20]. In sol-gel applications, it is reported that ILs have served as solvents [21, 22], pore templates [23, 24], drying control agent [25] and catalyst [26]. Zhang et al., synthesized silica gel materials with various RTIL as template and concluded that the increasing in alkyl chain length of imidazolium cation resulted in the increase of pore size of the silica materials [27]. The properties of ILs can be significantly changed with the various combination of cation and anion. Thus, the diversity of the selected ILs as the template in sol–gel synthesis can have important effect on the properties of the obtained porous materials [28].

In this study, Ionic Liquid (IL) mediated sol-gel silica adsorbents were prepared and used for the removal of Cr(VI) ions from aqueous solution. Three different types of ILs such as Aliquat 336$^{®}$, EMIMTf$_2$N and [A336][NO$_3$] were incorporated onto silica adsorbents by following the one-step sol-gel process. Physicochemical and morphological characterizations of prepared adsorbents have been investigated by Fourier Transform Infrared Spectroscopy (FTIR) Scanning Electron Microscopy (SEM), Brunauer Emmett Teller (BET) analysis. In addition, thermal behaviors of prepared adsorbents were also characterized by Thermogravimetric Analysis (TGA). The sorption behaviors of adsorbents were investigated by a series of batch sorption experiments. Effect of the type of ILs on the adsorption performance was investigated as well as sorption percentages.

2. Materials and Methods

2.1. Materials

In this study, tricaprylylmethylammonium chloride (trade name Aliquat 336®, (C8H17)3CH3NCl), 1-Ethyl 3-methylimidazolium bis(trifluoromethylsulfony) imide [EMIMTf2N] and tricapryl methyl ammonium nitrate [A336][NO3] were used as ionic liquids. [A336][Cl] and EMIMTf2N were obtained from Sigma Aldrich, [A336][NO3] was synthesized by anion metathesis reaction. Tetraethyl ortosilicate with the chemical formula of Si(OC2H5)4 (TEOS) was used as a precursor for obtaining SiO2 matrix. Required concentration of chromium solution was prepared by using potassium dichromate salt, K2Cr2O7. Also, 0.1M of HCl and 0.1 M of NaOH solutions were used to adjust the pH of the solution. Chemical structures of commercial ionic liquids are shown in Figure 1.

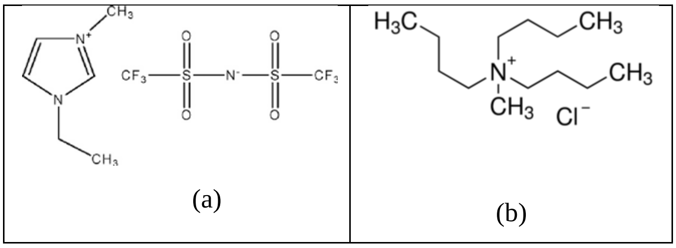

(a)
(b)

Figure 1. Chemical structures of commercial ionic liquids a) EMIMTf$_2$N b) Aliquat 336$^{®}$.

2.2. Synthesis of the task specific ionic liquid

A336 [NO3] (task specific IL) was synthesized by anion metathesis reaction of Aliquat 336® with KNO3 solution. Reaction can be given as follows;

A336[Cl] + KNO3 ⟶ A336[NO3] + KCl

Ionic liquid (A336[Cl]) and 2 M of KNO3 solutions were contacted for 1 hour by 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- ion content of the ionic liquid by using AgNO3 solution.

2.3. Adsorbent preparation

Sol-gel process was used for the preparation of sorbents based on nanoporous silica oxide matrices in whose interconnected network, ionic liquid got trapped. In this manner, 5 mL of TEOS as a silica precursor and 2.5 mL of EtOH were mixed in an ultrasonic media. And various amount of IL (0-14%) were added into TEOS-EtOH solution and mixed at 40°C during 30 min. Then, 2.5 ml of aqueous HCl solution (37 wt %) was added as dropwise and the solution was mixed during futher 2 hours. Then, the solution was poured into the moulds and left to dry at ambient conditions. Finally obtained products was ground into powders for the subsequent characterization and adsorption studies. Prepared sorbents are abbreviated according to type of IL, as given in Table 1.

Table 1. Nomenclature of prepared silica adsorbents

ID	Ionic Liquid
SG-Ø	-
SG-A	Aliquat 336®
SG-TS	[A336] [NO_3]
SG-IL	[$EMIMTf_2N$]

2.4. Characterization

The functional groups of the prepared adsorbents were investigated by using a Fourier Transform Infrared spectrometer (FTIR-Pelkin Elmer Spectra 100) in the wave number range of 650-4000 cm^{-1}. The surface morphology of adsorbents was investigated by using Scanning Electron Microscope (SEM). The microscope was operated at an accelerating voltage of 20.00 kV. The particles were coated with a gold layer in order to make them conductive. Surface area and pore volume of silica adsorbents were analyzed by Brunauer–Emmett–Teller (BET) in Micromeritics Gemini V model. Thermal Gravimetric Analysis (TGA) was carried out using Perkin Elmer Diamond TG/DT model to investigate the thermal behavior of the silica particles.

2.5. Batch sorption studies

The adsorption of Cr (VI) ions from aqueous solutions onto the silica based adsorbents was investigated by a series of batch sorption tests to obtain the adsorption performances of adsorbents as removal percentage.

For the batch adsorption studies, solution varying concentration (50-700 mg/L) of Cr(VI) were equilibrated with 50 mg of adsorbents by shaking at 150 rpm using a NUVE model ST 30 water-bath shaker. After equilibration, the adsorbents were removed and the supernatants were analyzed for Cr(VI) concentration by using Atomic Absorption spectrophotometer (Perkin Elmer, Varian 10 +) (AAS). The percentage of Cr(VI) removal R(%), was calculated by using the following expression:

$$R(\%) = \frac{(C_0 - C_e)}{C_0} 100 \qquad (1)$$

where C_0 and $C_e$are the initial and equilibrium concentrations (mg/L), respectively. Equilibrium concentration represents the concentration value where the adsorption isotherm reaches plateau.

The adsorption capacity of the prepared adsorbents was evaluated using the following equation:

$$q_e = \frac{(C_0 - C_e)\, V}{m}$$

where q_e is the adsorption capacity (mg/g), C_0 and $C_e$are the initial and equilibrium concentrations (mg/L), respectively. V is the volume of Cr(VI) solution and m is the mass of dry adsorbent

3. Results and Discussion

3.1. Characterization

3.1.1. Chemical characterization- FTIR analysis

FTIR spectrums of the untreated silica, ionic liquid confined silica and bulk ionic liquids are shown in Figure 2.

In the FTIR spectra of untreated silica materials (SG-Ø) (Figure 2 a), typical indication of silica structure are observed with the peaks of Si—O—Si groups appeared at 1060 and 790 cm^{-1} wavelengths. In addition, the peak at the wavelength of 947 cm^{-1} is assigned to the vibration of Si-OH which remarks the hydroxyl group of the particle surface. Another peak at 3259 cm^{-1} wavelength can also be attributed as the indication of unreacted –OH structure. At this wavelength, –OH peaks are decreased or disappeared with the incorporation of ionic liquid due to the replacement of hydroxyl group of silica structure with the organic group of ionic liquids.

The FTIR spectrum of [A336][Cl] (Figure 2.c), the peaks around the position of 2923 cm^{-1} can be attributed to the characteristic absorption of -CH3 of alkyl chain and peaks at the position of 1466 and 1378 cm^{-1} are based on the structure of quaternary ammonium moiety of the ionic liquid. The peak located at 1465 cm^{-1} (Figure 2 b) is pronounced functionalization of silica particles with [A336][Cl] type ionic liquid.

Peaks appeared at 3159 and 1574 cm^{-1}wavelengths (Figure 2 e) can be attributed as the C=N bonds of the imidazolium ring. Also, the bands around 1067 and 795 cm^{-1} indicate the asymmetric and symmetric stretching of Si—O—Si vibration, respectively. These data are the important indications for the ionic liquid presence in SG-IL structure.

The peaks around the position of 2924 cm^{-1} can be attributed to the characteristic absorption of -CH3 of alkyl chain and the bands between 1467 and 1328 cm^{-1} are based on the structure of quaternary ammonium moiety of the ionic liquid. The peak located at 1326 cm^{-1} (Figure 2 f) is pronounced functionalization of silica particles with [A336][NO3] type ionic liquid.

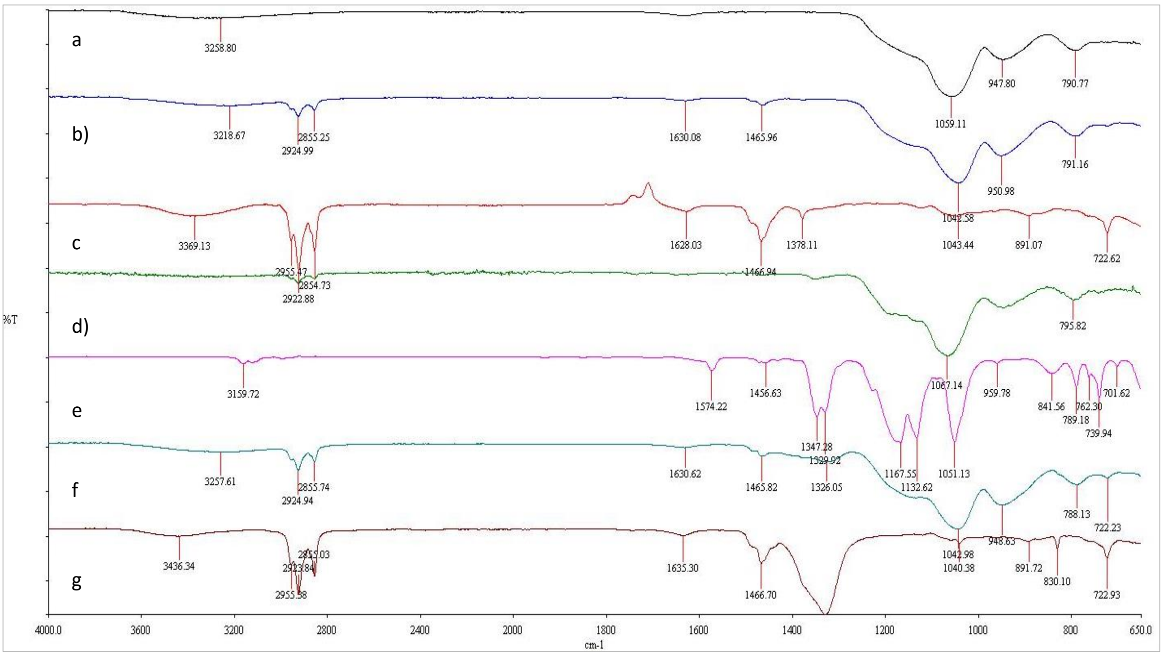


Figure 2. FTIR spectra of ionic liquid functionalized silica based adsorbents a) before functionalization (SG-Ø) b) adsorbent (SG-A) functionalized with [A336][Cl] c) ionic liquid [A336][Cl] (Aliquat 336) d) adsorbent (SG-IL) functionalized with EMIMTf$_2$N e) ionic liquid EMIMTf$_2$N f) adsorbent (SG-TS) functionalized with [A336][NO$_3$] e) ionic liquid [A336][NO$_3$]

3.1.2. Surface properties- BET analysis

BET surface area [m^2/g] and pore width [nm] values of silica based and ionic liquid functionalized silica adsorbents are shown in Table 2.

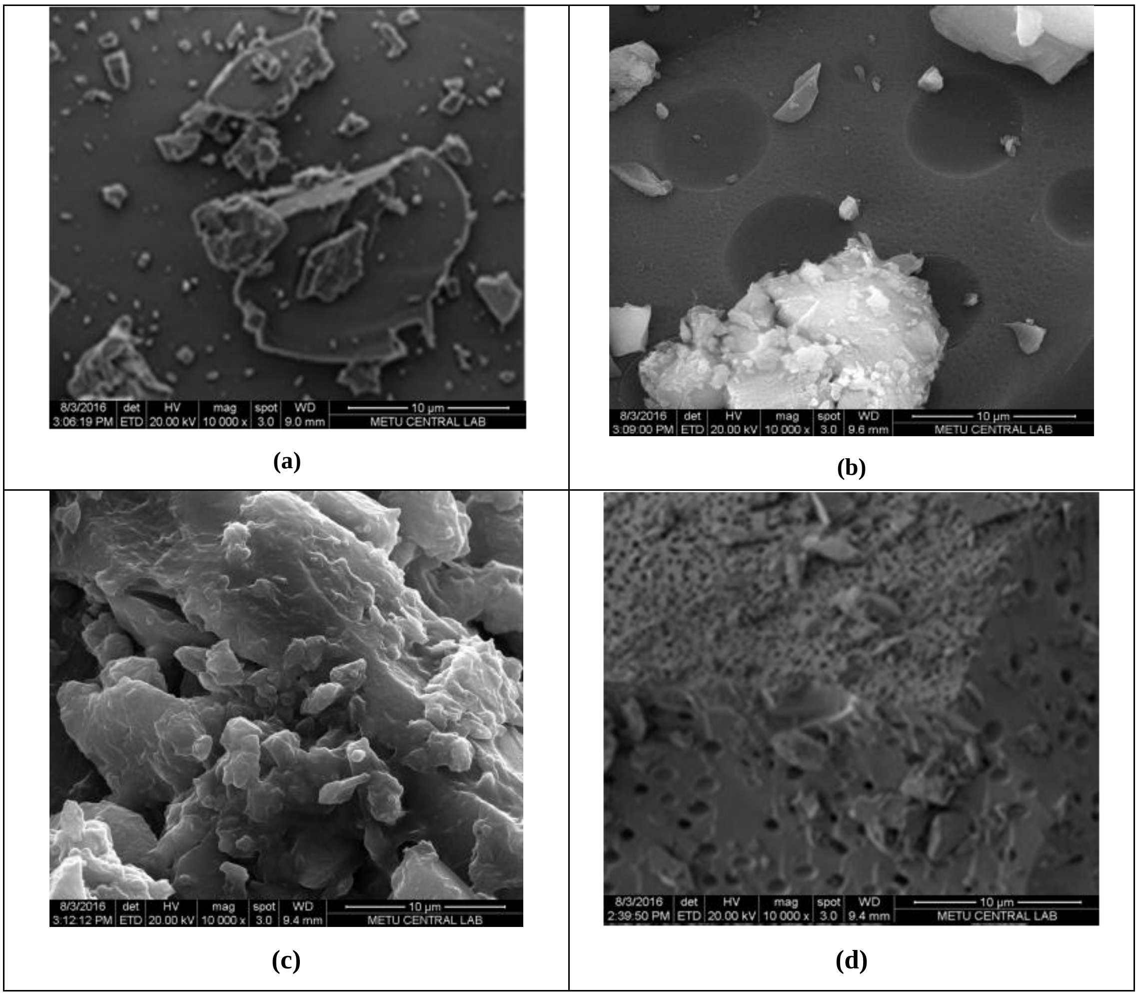
Table 2. BET analysis data of prepared adsorbents.

Adsorbents	Surface Area [m^2/g]				Pore Volume [cm^3/g]	Pore Size [nm]
	BET	Langmuir	t-Plot Micropore	t-Plot External		
SG-Ø	577	744	148	428	0.30	2.13
SG-IL	299	402	-	372	0.23	3.07
SG-TS	593	755	-	-	0.34	2.07
SG-A	602	762	-	-	0.32	2.03

As shown in Table 2. silica based adsorbents functionalized with various type of ILs were characterized to be mesoporous with average pore diameter of 2 nm and BET surface area in the range of 300 -600 m^2/g. Pore volumes of SG-TS and SG-A are higher than SG (untreated) type adsorbents while average pore diameters of adsorbents containing TS and A type ionic liquids are lower than SG leading to higher surface area. On the other hand surface area of SG-Ø adsorbents decreases with modification with IL type ionic liquids. This may be attributed that the surface area is occupied by the long alkyl chain of EMIMTf$_2$N type ionic liquid.

3.1.3. Morphological characterization- SEM analysis

The morphological characteristics of SG-A, SG-TS and SG-IL were evaluated respectively using a Scanning Electron Microscopy (SEM) as shown in Figure 3.



(a) **(b)**

(c) **(d)**

Figure 3. SEM images of prepared adsorbents with the magnification rate of 10000 a) SG-Ø b) SG-A c) SG-TS d) SG-IL.

In the SEM images of silica materials having none IL content (SG-Ø), it is observed that, the surface area of SG has nonporous and nonhomogeneous structures. Pore structure formation is observed by presence of the ionic liquid especially Aliquat 336 ®, [A336][Cl], (SG-A) and imidazolium based IL, EMIMTf$_2$N, (SG-IL). From the SEM images it can be concluded that ionic liquids acted as porogens in the preparation of silica adsorbents.

3.1.4. Thermal behavior analysis- TGA

Thermal stability of the bulk IL and silica based adsorbents containing various amount of ILs are shown in the Figure 4.

In TGA thermograms (Figure 4), it is clearly observed that decomposition temperature (T$_d$) of bulk IL ([EMIM][Tf$_2$N]) is at about 400 °C and silica adsorbents without IL content (SG-Ø) is started to decompose at low temperatures around 50 °C. The adsorbents containing imidazolium based ionic liquid with the weight percentages of 20 and 40 %, show increase in T$_d$ compared to pure silica adsorbents (SG-Ø). It can be concluded that, thermal stability of prepared adsorbents increased upon confinement of ILs.

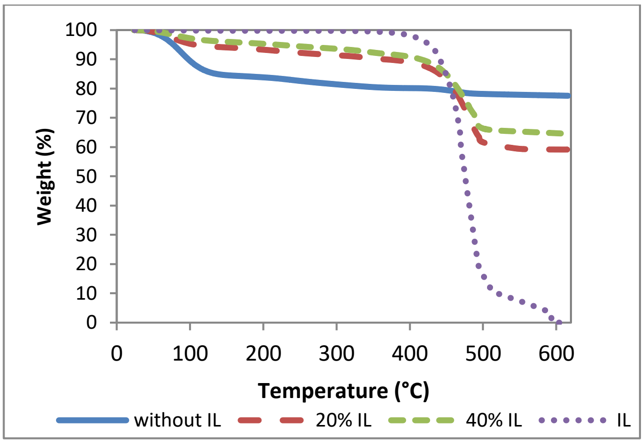


Figure 4. TGA thermograms of SG-IL adsorbents.

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

Sorption performances of silica based adsorbents containing various amount and type of ionic liquid were evaluated as the removal percentage of Cr(VI) ions from aqueous solution. Effects of ionic liquid amount were also examined by using two different ratio of ILs on the mass basis such as 0.5 and 0.7 g-IL/g-silica precursor. Results are shown in Figure 5.

It can be confirmed from Figure 5 that SG-TS and SG-A type adsorbents showed a better removal performance for Cr(VI) in comparison to untreated silica adsorbent (SG-Ø). Although the results of SG-A and SG-TS exhibited quiet similar results, SG- A can be chosen as adsorbent for the further studies. Because of the fact that SG-TS needs additional step for synthesis of ionic liquid comparing with the preparation of SG-A .

Sorption percentages of the adsorbents have been enhanced by containing Aliquat 336® type ionic liquids (SG-A) up to 99%.

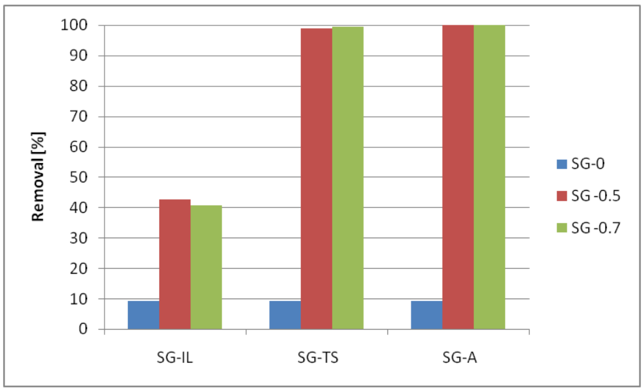


Figure 5. Removal efficiency of silica based adsorbents synthesized by using various type of ionic liquids for the sorption of Cr (VI) ions.

Adsorption capacity of SG-A type adsorbents was calculated as 31.74 mg/g and it is also observed that increase in IL content has no pronounced effect on the sorption performances.

The adsorption capacity of ionic liquid (Aliquat336®) incorporated into sol-gel silica adsorbent (SG-A) is compared with the capacity of the novel materials synthesized in the other studies as shown in Table 3.

Table 3. Comparison of Cr(VI) adsorption capacities of different adsorbents reported in literature

Adsorbent	Capacity (mg/g)	References
Maghemite nanoparticles with polyrhodanine	13.51-25.85	28
Nanoporous activated neem bark	21.28	30
Carbon/AlOOH composite	25.64	31
p(AN-co-APTMACl) hydrogel	18.16	32
Hybrid cellulose aerogel (ZIF@CA)	41.80	33
Expanded graphite/layered double hydroxides (EG/LDHs) nanocomposites	13.44	34
Mgnetic titanium nanotubes coated phosphorene (MNP-PN-TNT)	35.00	35
Ionic iquid (Aliquat 336) incorporated sol-gel silica (SG-A)	31.74	Present study

As indicated in Table 3., SG-A adsorbent exhibits higher adsorption capacity than most of the adsorbents previously reported in literature. Therefore, It can be concluded that the silica based adsorbent incorporated with ionic liquid is a very promising material for the removal of Cr(VI) ions.

4. Conclusion

In this study ionic liquid mediated sol-gel silica adsorbents are prepared for the removal of Cr (VI) ions from aqueous solutions. Physicochemical and morphological characterization of prepared adsorbents concluded that ionic liquids acted as porogens and increased the thermal stability of the silica based adsorbents.

Based upon the experimental results, Cr(VI) sorption percentages achieved with silica adsorbents containing ionic liquid were higher than that of untreated adsorbents due to synergistic effect of electrostatic interaction with IL and Cr(VI) ions. Sorption percentages of the adsorbents were enhanced by containing ILs up to 99% with the adsorption capacity of 31.74 mg/g. It can be concluded that sorption of Cr(VI) ions from aqueous solution by sol-gel silica based adsorbents containing Aliquat 336® takes place favorably and these type of adsorbents are very prospective materials for the adsorption of Cr (VI) from aqueous streams.

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Conflicts of interest

The authors state that did not have conflict of interests

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