

Borosilicate glasses modified with organic ligands: A new selective approach for the removal of uranyl ion

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Abstract

Barium borosilicate glass was found to have high uptake capacity for many cations. To improve its selectivity, surface modification was carried out. In order to make the glass selective towards uranyl ion, organic ligands like tri-*n*-octylphosphine oxide (TOPO) and 8-hydroxy quinoline (Oxine) were used. It was observed that the surface modification resulted in the change in uptake property of the glass. The uptake process was faster and within 5 h, 90% of the uranyl ion could be taken up from a 0.01 mM solution. With use of the modified barium borosilicate glass and EDTA as masking agent, uranyl ion could be selectively removed from mixtures of cations.

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1. Introduction

Separation of metal ions from a mixture of cations and selective removal of a particular cation from an aqueous stream are of interest in a variety of fields, such as the recovery of precious metal ions from the waste, hydrometallurgy, removal of toxic metals from the environment [1,2], etc. Selective separation of uranium from a source containing the metal ion at low concentration level has attracted the attention of many chemists because of its importance in nuclear industry. There are reports dealing with separation of uranyl ion using different techniques [3,4].

Therefore these needs have led to the development of various technologies for effecting the removal of these metal ions from aqueous effluents. The most commonly used techniques involve processes like chemical precipitation, adsorption, electrolysis, ion exchange, reverse osmosis, etc. [5]. Adsorption

techniques, using a number of organic, inorganic, natural, synthetic, activated or modified model adsorbents, are the most widely employed procedures in the waste treatment studies as these provide low-cost alternatives and are effective adsorbents [6–8]. However, further alternatives are always being sought after and on going research in this field is of great interest and value to many a researchers.

Borosilicate glasses are technologically important due to their high mechanical strength and chemical durability and are widely used in various applications. In nuclear industry it is mainly used as matrix for immobilizing the radioactive ions present in the waste generated from the nuclear reactors [9–11]. The structural elucidation of these glasses has been carried out using magic angle spinning nuclear magnetic resonance (MAS NMR), Raman and IR spectroscopy [12–15]. These studies show the existence of structural units like trigonally coordinated boron (BO₃), tetrahedrally coordinated boron (BO₄), silicon structural units having different number of bridging oxygen atoms, (Q^{*n*} denotes Si with *n* number of bridging oxygen atoms). Addition of network modifiers (alkali/alkaline earth metal oxides) to borosilicate glasses results in the conversion of BO₃ to BO₄ structural

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units. The $(\text{BO}_4)^-$ and $(\text{SiO}_4)^-$ structural units are charge neutralized by Na^+ ion, which can be replaced by other ions.

There are reports wherein the nature of the metal ions present in the glass matrix has been studied in detail. These ions were leached out and analyzed [16,17]. In our earlier study, it was seen that barium borosilicate glass (BBS) showed an increased sorption for uranyl and strontium ions as compared to sodium borosilicate glass (SBS). This was attributed to the fact that the addition of barium oxide as modifier to SBS resulted in the increase in the number of non-bridging oxygen atoms in the structure. This is seen from ^{11}B and ^{29}Si MAS NMR studies which showed an increase in the number of $\text{Si}-\text{O}^--\text{Na}^+$ and $\text{B}-\text{O}^--\text{Na}^+$ structural units in BBS and thus the increase in ion exchange capacity for the same [18].

In this paper, the use of BBS glasses for the separation of uranyl ion from a mixture is being reported. In order to achieve selectivity, modification and impregnation techniques have long been to bring about selective removal of a particular ion [19–21]. In this work, a similar approach has been adopted for the modification of the glass surface using organic ligands. The choice of these organic ligands is based on the knowledge of solvent extraction. It is well known that tri-*n*-octyl phosphine oxide (TOPO) and butyl phosphates have been used frequently for the extraction of lanthanides and actinides [22,23]. Hence based on these reports, it was decided to make use of these reagents for the modification of BBS glass samples. To the best of our knowledge, this is for the first time such an attempt has been made on barium borosilicate glasses.

2. Experimental

2.1. Reagents

- Uranyl ion solution was prepared using uranyl acetate obtained from E. Merck. Appropriate amount of the salt was weighed and dissolved in small amount of nitric acid and made up to the volume using distilled water.
- Transition metal ion solutions were prepared by dissolving the appropriate amounts of the chloride salts (obtained from S.D. Fine Chemicals Ltd., India) in dilute acid and made up to the volume using distilled water. The solutions were standardised by titration with EDTA using a suitable metallochromic indicator [24].
- Tri-*n*-octylphosphine oxide and 8-hydroxy quinoline (Oxine), obtained from E. Merck, Germany were used as received.
- Analytical reagent grade $\text{Ba}(\text{NO}_3)_2$, NaNO_3 , SiO_2 and H_3BO_3 were used for synthesis of glass samples.

2.2. Instrumentation

The absorbance measurements were carried out with a UV-Vis double beam spectrophotometer using a 1 cm quartz cell. The pH measurements were carried out using an EIL 7030 pH meter equipped with a combination electrode.

2.3. Procedure

- Synthesis of glass samples: Required amounts of analytical grade $\text{Ba}(\text{NO}_3)_2$, NaNO_3 , SiO_2 and H_3BO_3 were ground well and heated at 1000°C for 4 h in siliminite crucibles. The free flowing melt was quenched between two stainless steel plates. The glass samples were characterized using different techniques like XRD and NMR [25]. The determination of chemical composition of the glass is carried out as follows. A known weight of glass was treated with hydrofluoric acid and warmed. The resultant solution was then boiled with perchloric acid to remove excess HF. Once all HF is removed, the solution is evaporated to dryness and then nitric acid was added and made up to a known fixed volume and analyzed for Na^+ and Ba^{2+} ions by atomic emission spectroscopy (AES). In order to analyze the silicon and boron content, a known weight of glass was fused with sodium carbonate at 1100°C in a platinum crucible. The residual mass was dissolved in nitric acid and the solution was analyzed by AES.
- Modification of the glass: A known weight of glass was added to 0.01 M solution of the organic ligands and shaken continuously for 5 h. The samples were then left in the solution overnight. The glass sample was then centrifuged, washed, dried and used for further experiments. The modified glass samples thus obtained are referred to as L-BBS.
- Sorption studies: The ion exchange studies were carried out in batch mode. A known weight of glass sample was equilibrated with 10 ml of metal ion solution at a particular pH for a known period. The solution was then centrifuged and the filtrate was analyzed for the metal ion.
- Recovery of metal ions: The recovery studies were carried out by stripping the sorbed metal ion from the glass using dilute acid. For this, it was seen that 0.01 M HCl was efficient in stripping out the ions.

3. Results and discussion

The molar compositions of samples of sodium borosilicate and barium borosilicate are given in Table 1. The determined chemical composition of glass was in good agreement with the nominal composition.

The single ion studies on the uptake of Cu^{2+} , Zn^{2+} and UO_2^{2+} were carried out using unmodified BBS and SBS samples. It was seen that the uptake efficiency of BBS was much higher as compared to SBS. Hence all further studies were carried out using BBS only. The results of this uptake showed that in the concentration range of up to 3 mM, the all the ions are taken up to an extent of more than 95% and there exists no

Table 1
Molar composition of various components of the two glass samples

Glass sample	Mol%			
	SiO_2	B_2O_3	Na_2O	BaO
SBS	53.53	30.30	16.17	–
BBS	47.34	26.80	14.30	11.56

selectivity. In order to achieve selectivity amongst these ions, EDTA was used as a masking agent. It is seen that on addition of EDTA, the amount of the metal ions taken up reduced drastically. It is seen that the amount of uranyl ion taken up was about 20%, whereas the amounts of Cu^{2+} and Zn^{2+} ions taken up was less than 10%. This is because EDTA forms a weaker complex with uranyl ion ($\log K=7.4$) as compared to Cu^{2+} and Zn^{2+} ions ($\log K$ values are 18.9 and 16.5 respectively). A synthetic mixture containing these three ions of equal concentrations was treated with BBS glass sample. It was seen that in presence of EDTA as masking agent, selectivity with respect to uranyl ion could be achieved but however, the uptake was around 50%.

3.1. Need for modification

It is seen from the single ion studies that the BBS samples could not be used for the selective uptake of uranyl ion even upon addition of masking agents in the aqueous solution. In order to achieve improved and selective uptake, it was thought of modifying the glass with organic ligands. The removal and recovery of metal ions has a potentially vast range of applications in conserving environment and using resources. In this regard, the chelate-forming polymeric and copolymeric ligands have been extensively studied and many reviews are available in the field [26–30]. These polymeric and copolymeric materials have been used for the preconcentration and separation of trace elements from seawaters; in particular, the inclusion of diprotic acid units copolymeric matrices as the complexation centers results in promising materials for the separation of heavy metal ions from aqueous solution [31]. The use of these polymeric adsorbents for preconcentration and further determination of these ions at trace levels have also been reported [32,33]. All these studies deal with the synthesis of polymeric beads with suitable functional group to make the adsorbent selective to ion of interest (uranyl).

However, in the present study, the glass is modified by the incorporation of simple organic ligands. The BBS samples modified with organic ligands (L) are referred to as L-BBS. The ligands selected are those which have good complexing ability with the uranyl ion. For the present study, two organic ligands, namely oxine and tri-*n*-octylphosphine oxide (TOPO), were used. These two reagents are well-established complexing agents for uranyl ion. It is reported that tri-*n*-octylphosphine oxide [22,23] has been used frequently for the extraction of lanthanides and actinides. Hence, based on the complexation chemistry in solution, it is expected that the ligands incorporated in the glass matrix will complex with uranyl ion present in solution.

The incorporation of these ligands on the barium borosilicate glass has been confirmed by further studies. The uptake of oxine by unmodified glass showed that there capacity of BBS for oxine is 1.5 mmol/g. This indicates that the oxine is incorporated well into the glass matrix. The uptake of Cu^{2+} ions by oxine-modified glass showed the formation of yellow colour on the glass surface. This colour could not be removed after repeated washes. This confirmed that the Cu^{2+} –oxinate complex was formed well

within the glass matrix. Based on the results, it was assured that the modified ligands are incorporated well into the matrix and can be used for uptake studies.

3.2. Effect of contact time

The percentage of metal ions removed as a function of time is given in Fig. 1. All the data given in the figure are average of duplicate measurements with an error of around 5%. The studies were carried out using 0.01 mM metal ion solutions. It is seen that the metal uptake of L-BBS modified glasses is much faster as compared to the unmodified samples. The results show that a contact time of 5 h was found suitable for the removal of all the metal ions, whereas for BBS, an equilibration period of 24 h was needed for near-complete removal of uranyl ion of the same concentration.

3.3. Effect of pH

Since the surface charge of an adsorbent could be modified by changing pH of the solution, pH is one of the most important parameters affecting the adsorption process of metal ions. In order to know the influence of this parameter on the adsorption of metal ions, all the samples were equilibrated with single metal ion solution at different pH values ranging from 2 to 8 for 5-h period and the concentration of the metal ions left in solution were determined. The average results of duplicate experiments are presented in Fig. 2 with an error of 5%. It is seen that for L-BBS, the percent adsorption increased with increase in pH. For unmodified glass samples (BBS), the adsorption increases to a particular value and then decreases with increasing pH. This is in accordance with our earlier work using BBS glass for uranyl ion sorption [18]. At lower pH values (<3.0), the active sites of the adsorbent are less available for the metal ions due to protonation of the active sites at higher H^+ concentration. With increase in pH values it is seen that for L-BBS, the adsorption is higher because the complex formation is much stronger than the hydrolysis of metal ions. Hence all further studies were carried out at pH 5.

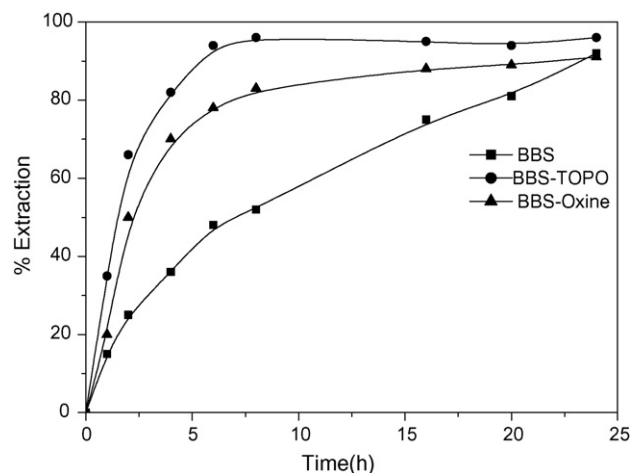


Fig. 1. Effect of contact time on uptake of uranyl ion (0.01 mM).

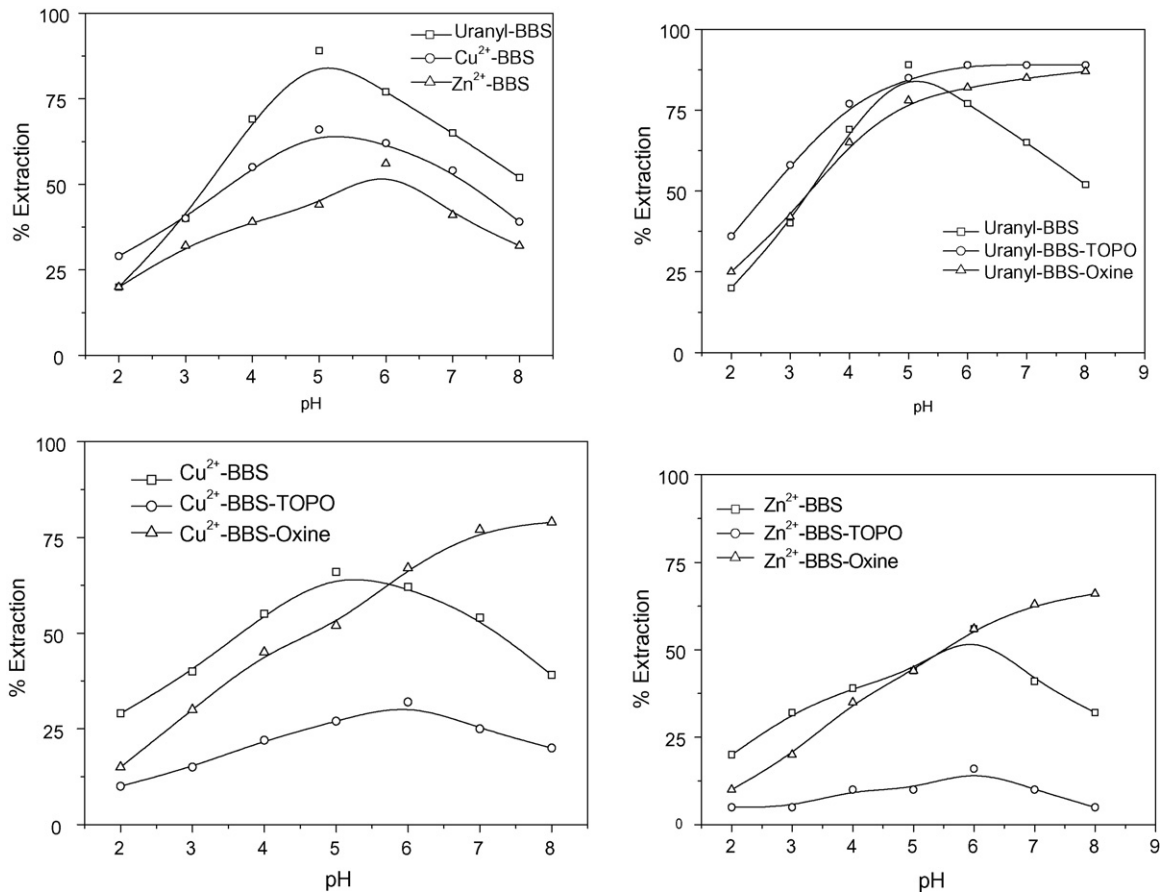


Fig. 2. Effect of pH variation on the amount of uptake for different systems.

3.4. Effect of adsorbent dosage

The effect of the adsorbent dosage on the removal of metal ions was studied by varying the amount of the glass sample from 0.02 to 0.2 g in 10 ml 0.01 mM solution at pH 5 for a period of 5 h. The variation of amount taken up with adsorbent dosage is shown in Fig. 3. It is observed that at the initial stages, there is a rapid increase in the uptake of metal ions with increase in the

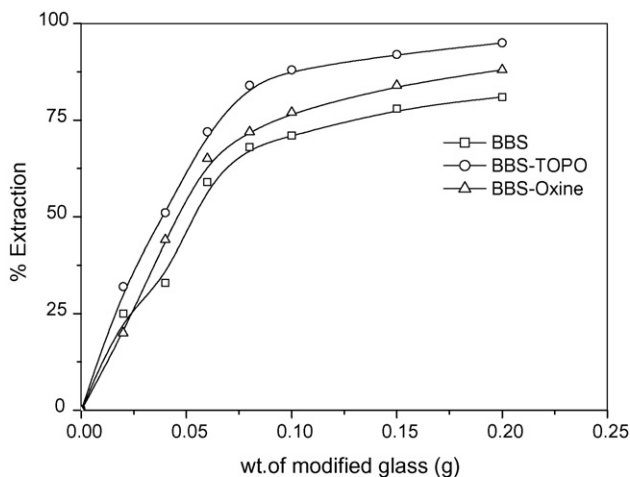


Fig. 3. Effect of adsorbent amount for uptake of uranyl ion (0.01 mM).

adsorbent dosage. This is expected because with the increase in the adsorbent amount, the ratio of the number of the adsorbent particles to metal ions increases. This results in more ions attached to the adsorbent surfaces.

3.5. Selectivity studies

Single ion studies were carried out using 0.1 and 0.01 mM metal ion solutions and modified barium borosilicate glass samples (L-BBS). The results for 0.01 mM solutions are shown in Table 2. At higher concentration level, the same trend is obtained but the actual uptake is slightly reduced. In order to understand the effect of modification of barium borosilicate glass, the results for the lower concentration is given. From the table, it is seen that

Table 2
Uptake of metal ions from single ion solutions

Metal ion	% Uptake				
	BBS		L-BBS		
	Oxine as modifier		TOPO as modifier		
	Without EDTA	With EDTA	Without EDTA	With EDTA	
Cu ²⁺	90	92	25	30	10
Zn ²⁺	80	90	30	20	10
UO ₂ ²⁺	95	92	80	95	90

for unmodified BBS samples, the amount of metal ion taken up is greater than 80%. Modification of BBS with oxine enhances the uptake and thereby reduces the selectivity further. This is because the three ions Cu^{2+} , Zn^{2+} and UO_2^{2+} form strong complexes with oxine with very high formation constants ($\log K$ values are 23.4, 16.7, 20.8 respectively). On addition of EDTA as masking agent to the solution containing the metal ions, there is an improvement in the selectivity. It is seen that the 80% of uranyl ion taken up by the oxine modified glass in presence of EDTA as masking agent in solution. However, the uptake of Cu^{2+} and Zn^{2+} ions is less than 20%. This is because both Cu^{2+} and Zn^{2+} ions form very strong EDTA complexes ($\log K$ being 18.9 and 16.5 respectively) as compared to uranyl ion ($\log K = 7.4$). The formation of anionic EDTA complexes in solution reduces the uptake by oxine-modified glass. Since the uranyl ion forms a weaker complex, it is taken up to a greater extent as compared to Cu^{2+} and Zn^{2+} ions.

In order to achieve selective uptake of uranyl ion, the barium borosilicate glass was modified using tri-*n*-octylphosphine oxide. The uptake studies with this glass showed that there was a significant selectivity in the uptake of uranyl ion even without the addition of EDTA in the solution. The amount of uranyl ion taken up is around 90% and the interfering ions (Cu^{2+} and Zn^{2+}) were taken up to an extent of about 30%. However, on the addition of EDTA to the metal ion solution, it was seen that the uptake of Cu^{2+} and Zn^{2+} ions was reduced further (<10%). Hence it is seen that by the use of EDTA as masking agent in the solution and TOPO as a surface modifier, uranyl ion could be selectively taken up.

The above results of single ion studies were made use of for the separation studies using binary mixtures with EDTA and L-BBS. In the present study, a representative synthetic mixture of uranyl ion is taken. The metal ions chosen are those, which are expected to interfere with uptake of uranyl ion. The main aspect of the present work is to reduce these interferences by modification using suitable organic ligands. The results of these studies are shown in Table 3. It is seen that in presence of equimolar concentrations of uranyl ion and interfering ions ($\text{Cu}^{2+}/\text{Zn}^{2+}$), the uranyl ion uptake is around 90% in both the cases. However, the % uptake of the interfering ions is around 20% in case of oxine-modified BBS and the same reduces much to an extent of about 10% when TOPO is used as the modifier. It is interesting to note that in presence of much excess of interfering ions, the amount of uranyl ion taken up is not affected. It is the amount of these ions taken up that are affected to a slight extent at high

concentration levels, especially in the case of oxine-modified BBS.

The concentrations taken in the present study are higher than in actual samples like seawater wherein the concentration of UO_2^{2+} , Cu^{2+} and Zn^{2+} are 3, 3 and 10 ppb (ratio of 1:1:3) as cited in literature [34,35]. In the present study, although the concentration levels of the three ions are much higher than that in seawater, the ratio of the three ions has been maintained as in the seawater. It is seen that even at higher concentration levels, there is no interference on the uranyl ion uptake by other ions. Therefore, it may be possible to use the present system for preconcentration of uranyl ion present at low concentration.

4. Conclusion

It is seen that the selectivity of borosilicate glass is improved by modification using organic ligands like oxine and TOPO. The use of EDTA as masking agent in solution results in improved and selective removal of uranyl ion. The use of TOPO makes the borosilicate glass more superior to oxine-modified glass. The uranyl ion uptake is as high as 90%. To evaluate the usefulness of this study to actual seawater sample, different aspects have to be considered. First and foremost, the very high concentration of NaCl in the actual sample will not interfere with the uranyl ion uptake because the ligands incorporated do not form complexes with Na^+ . Moreover, the glass has Na^+ ions in its matrix. The presence of bicarbonate may cause slight reduction in uptake but the use of a more selective ligand like TOPO may improve the uptake from an actual sample.

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Table 3
Interference studies using different binary mixtures using L-BBS in combination with EDTA as masking agent

A	[A]:[UO_2^{2+}]	% of uranyl ion taken up		% of metal ion taken up	
		Oxine	TOPO	Oxine	TOPO
Cu	1:1	80	91.81	15	<1.0
	100:1	74	91.42	25	5
Zn	1:1	88	90.96	10	<1.0
	100:1	75	90.82	20	10

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