Studies on the crystallographic changes in an analogue of aluminosilicate mineral Muscovite on sorption of \( \text{UO}_2^{2+}, \text{Th}^{4+} \) & \( \text{Ru}^{3+} \)

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An analogue of aluminosilicate mica mineral Muscovite has been synthesized hydrothermally at 200°C and sorption studies performed for \( \text{UO}_2^{2+} \), \( \text{Th}^{4+} \) and \( \text{Ru}^{3+} \) at room temperature in acidic medium (0.1 M). The X-ray diffractograms and scanning electron micrographs have been used to verify changes in crystallinity and crystal morphology on sorption. The synthesized gel has been characterized by X-ray powder diffraction, energy dispersive spectrometry, thermogravimetric analysis, FT-IR spectroscopy and scanning electron microscopy. The chemical composition of the gel is found to be \( \text{K}_4\text{Al}_{12,5}\text{Si}_{10,5}\text{Al}_{20,5}(\text{OH})_{24,5}\text{H}_2\text{O} \). Energy dispersive spectrometry (EDS) mapping indicates that metal ions are sorbed on the synthesized material by ion-exchange mechanism. Also, the structure of aluminosilicate mineral Muscovite is retained upon \( \text{UO}_2^{2+} \), \( \text{Th}^{4+} \) and \( \text{Ru}^{3+} \) sorption implying that surface and end sites are more affected upon sorption while the interlayer positions of the mineral are not engaged in metal ion sorption.

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Aluminosilicates with chemical, thermal and radiation resistivity, have received considerable attention in recent years in the recovery and recycling of aqueous radioactive wastes\(^{1,2} \). Aluminosilicates show high selectivity for certain radionuclides because they are natural ion exchangers and can be used in radioactive waste water treatment\(^{5,6} \). In general, the sorption reactions on minerals are expected to occur rapidly with ion-exchange taking place mostly at the surface and edge position of the clay. There may be a change in the crystallography of the material after the exchange process. However, the integrity of the clinoptilolite network is maintained in the sample when the zeolite cations are exchanged with radioactive cobalt ions\(^7 \). Thus, the purpose of this work is to study the effect of exchange of ions, viz. \( \text{UO}_2^{2+} \), \( \text{Th}^{4+} \) and \( \text{Ru}^{3+} \) on crystallinity and crystal morphology of the aluminosilicate mineral Muscovite.

Experimental

The synthetic analogue of the mica mineral Muscovite was synthesized by hydrothermal method using teflonlined stainless steel autoclave\(^{8,9} \) at 200°C for 72 h. The synthesized gel was characterized using different spectroscopic techniques, viz. X-ray powder diffraction (XRD), energy dispersive spectrometry (EDS), thermogravimetric analysis (TGA), FT-IR spectroscopy and scanning electron microscopy (SEM).

To confirm whether the crystallinity was maintained, the gel was characterized before and after the sorption of \( \text{UO}_2^{2+} \), \( \text{Th}^{4+} \) and \( \text{Ru}^{3+} \) by X-ray powder diffraction. The chemical composition of the synthetic gel was checked for the metals K, Al and Si using EDS test. To make it clear that, whether it is an ion-exchange phenomenon or not, EDS patterns were recorded before and after the sorption process. TGA was used to determine the number of water molecules in the framework of the gel. FT-IR spectrum (using NICOLET-410 spectrometer) of the sample was also recorded. The changes in crystal morphology were evaluated by SEM.

Results and discussion

Characterization

The results of X-ray powder diffraction patterns (Fig. 1a) of the sample shows maxima at 20 = 26.432 which corresponds to \( d = 3.369 \) Å. These values are in agreement with standard reported values. The broad peaks obtained in the diffractogram of the material show its amorphous character\(^{10,11} \).

The chemical composition of the synthesized gel obtained from energy dispersive analysis (Fig. 2a) for the metals K, Al and Si agrees well with the weight percentage of these metals. The TGA graph (Fig. 3) shows 10% weight loss has been obtained in the temperature range 40-240 °C and 18.56% weight loss in the range 240-680.56 °C. Ten percent weight loss corresponds to two water molecules and 18.51% weight loss corresponds to four hydroxyl group, suggesting that the hydrothermal phase has the composition \( \text{K}_4\text{Al}_{12,5}\text{Si}_{10,5}\text{Al}_{20,5}(\text{OH})_{24,5}\text{H}_2\text{O} \).

To confirm the presence of -OH group as well as the Si-O-Si, Si-O-Al and O-Si-O linkage in the synthesized material Muscovite, FT-IR analysis was
Fig. 1—X-ray diffractograms of: (a) hydrothermally synthesized Muscovite gel; (b) the same loaded with UO$_2^{2+}$; (c) Th$^{4+}$; (d) Ru$^{3+}$.

Fig. 2—EDS spectrums of: (a) hydrothermally synthesized Muscovite gel; (b) the same loaded with UO$_2^{2+}$; (c) Th$^{4+}$; (d) Ru$^{3+}$.
Thus, a luminos ilicate network is not destroyed, and the integrity of the network during ion-exchange is preserved. The XRD studies on synthesized and metal ion sorbed mineral also show that the structure of the mineral is retained upon sorption. The fact that the XRD peak intensity, peak position and peak shapes which reflect the extent of crystallinity of the mica mineral are almost unaffected, indicates that sorption takes place on the surface and edge position of the muscovite. This suggests that the inter-layer position of the mineral is not involved in metal ion fixation due to relatively strong binding force among the sheets. Thus, outer layer sites are much more affected during sorption than that inner sites whereas the small difference in 20 and d spacing values may be due to presence of exchangeable Al and K ions.

Energy dispersive spectroscopic studies
EDS analysis not only provides weight percentage of the elements but also provides evidence in favour of ion exchange process. This can be observed from the EDS analysis of the material before and after ion-exchange (Fig. 2). The EDS analysis indicates that K+ ions are completely exchanged with these rare earth metal ions. There is also decrease in the weight percentage of Al3+ ions, clearly showing that it is an ion-exchange process as the K+ ion peaks in EDS patterns are missing and there is decrease in the Al peak after sorption.

Scanning electron microscopy studies
To study the changes in the crystallography of the material after the exchange process, the SEM micrographs of the material before and after loading with UO22+, Th4+ and Ru3+ ions are recorded. The SEM micrographs (Fig. 5) clearly indicate that the...
crystal morphology of the material is influenced by the presence of exchangeable and exchanged ions. These SEM micrographs indicate that all those cavities which were empty, as indicated in Fig. 5a, get occupied after sorption / exchange process with metal ions sorbed at these places and also that nearly all the vacant sites present in the material before exchange are occupied by these ions on exchange\textsuperscript{17,18}.

The above study shows that the crystallinity of the synthesized gel is maintained in the sample when the cations are exchanged with any one of the UO\textsuperscript{2+}, Th\textsuperscript{4+} and Ru\textsuperscript{3+} ions from aqueous waste. The retention of the structure of muscovite upon UO\textsuperscript{2+}, Th\textsuperscript{4+} and Ru\textsuperscript{3+} uptake indicates that surface and edge sites are more effective in sorption. SEM micrographs also give evidence for the same.

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