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# Environmental Protection and treatment of Radio Active waste solutions in the Caspian sea using local clay minerals .

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#### Abstract

The aim of this work is to establish the optimum conditions for the removal of some radioactive elements from their waste solutions in the south west of the Caspian sea. In this respect an exploratory investigation is carried out using the clay minerals (kaolinite and vermiculite) to test the feasibility of its using for decontamination purposes and volume reduction. The different parameters affecting the sorption capacity of the radioactive elements of Cs-1%%, Co-% and Eu- $(1\Delta\%+1\Delta\%)$  by the investigated clay minerals have been studied. The uptake of the metal ion was determined for clay mineral-cation solution system as a function of contact time, pH, metal ion concentration and presence of some competing cations. Sorption data have been interpreted in terms of Freundlich equation. The presence of some organic complexing agents also affect the sorption process. The desorption of the investigated metal ions was also studied using different desorption solutions. The obtained data show that the clay mineral vermiculite can be considered as an efficient sorbent for metal cations from their aqueous solutions since the uptake efficiency is more than  $3\cdot\%$  for the three elements studied.

### **Introduction**

In view of the nuclear waste management, the sorption studies of radionuclides on various materials is of great importance and significance in evaluating the feasibility of a pariticular natural material for its using for the decontamination purposes and volume reduction. Many naturally occurring materials exhibit one or more of the useful sorption or chemical reactions with redioactive or stable trace elements. These natural materials are seldom \_ pure chemical species and thus anumber of different reactions may occur . sorption of various radionuclides on soils and clay minerals has been studied by several authors[1, 7]. The effect of synthetic organic complexing

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agents such as ethylenediaminetetracitic acid (EDTA) and diethylenetriaminepentacitic acid (DTPA), which are used as cleaning agents and decontaminants at nuclear research center, and organic complexing agents such as oxalates, ceitrates etc., present in soil and natural waters on the sorption of Cs ions have been investigated by Brouwer et al [ $\hat{r}$ ] on local soil contain illite as a principal clay [ $\hat{v}$ ].

The objectives of the present work are :

- a) Investigation of the mineralogical composition of some local clay mineral deposits
- b) Determination of the sorption capacity of the radioisotopes Cs  $_1^{\gamma \varphi}$ , Co  $_7^{\gamma}$  and Eu ( $_1^{\gamma \gamma + 1}^{\gamma \varphi}$ ) by the elected clay minerals.
- c) The desorption tendency of the investigated radioisotopes from the studied clay.
- Y. Determination of the Mineralogical content of the Investigated Clay Samples

In this work, two clay samples ( samples No.  $^{1}$  and  $^{7}$  ) were collected from the Anzali region . for the experimental studies , the samples were slightly ground to have a nearly homogenous material . The mineralogical analysis of the two investigated clay samples shows that Kaolinite and vermiculite are the most abundant minerals present in the two investigated samples.

# \*- Factors Affecting Sorption Of The Investigated Radioisotopes By The Clay Samples

۳, ۱.EFFECT OF CONTACT TIME

The variation of the metal sorbed (%) of the investigated cations by the clay samples, it is clear that the equilibrium is rapidly attained and a time of one hour is enough for the sorption reaction to reach the equilibrium [r]. The sorption of the investigated elements increases with time to reach a saturation level depending on the nature of the element and the type of the clay mineral. The metal sorbed (%) in case of vermiculite clay is more than 9.%.

# ۳٫۶.EFFECT OF METAL ION CONCENTRATION

The amount of ion sorbed per gram clay , X /m , in meq / g when plotted against the equilibrium carrier concentration [C] showed a straight \_ line relationship .These linear relationships indicate that the sorption process can be described by a Freundlich type isotherm [ $\gamma, \gamma$ ]

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# r,r. DEPENDENCE ON PH OF THE SOLUTION

The metal sorbed of the investigated elements  $Cs_{\gamma}^{\gamma}$ ,  $Co_{\gamma}^{\gamma}$  and  $Eu_{\gamma}(\lambda D \gamma + \lambda D \gamma)$ showed a gradual increase as pH increased with a maximum value of  $\beta$  while the metal sorbed for  $Eu_{\gamma}^{\gamma} + \gamma \Delta \gamma$  showed a relatively sharp increase as pH increased, with maximum values around  $\Delta, \gamma$  and then showed a light decrease to pH  $\lambda, \cdot$ . Generally, the metal sorbed (%) values obtained are in the order  $Eu_{\gamma}^{\gamma} + \gamma \Delta \gamma$ > $Cs_{\gamma}^{\gamma} + Co_{\gamma}^{\gamma} \cdot (at pH \Delta, \Delta)$ . The general increase in the sorption capacity with increasing the pH of the media can be discussed in the light of the exchange properties of the hydrogen ions and their effect on the solubility equilibria with different clay samples .Since the clay samples have exchange site of different binding energies, thus at low pH, the hydrogen competes for the available exchange sites and negatively affects the uptake of the different cations .As the pH increases, the hydrogen ion concentration decrease and the competitive effect of the proton with the metal cations decreases with subsequent increase in metal sorbed of the different cations

# ۳, ٤. EFFECT OF COMPETING ION CONCENTRATION

The effect of changing the concentration of foreign ions such as K, Mg and Fe on sorption of Cs  $_1 \%\%$ , Co- $\pounds$  and Eu\_( $1 \square \% + 1 \square \%$ ), resp., by the selected clay minerals was investigated .Only one competitive cation is considered for each radioisotope. the presence of K, Mg and Fe ions decrease the metal ion sorption of Cs  $_1 \%\%$ , Co  $_{\uparrow}$  and Eu  $_{(1 \square \%)}$ , respectively, by the two investigated clay minerals. This may be attributed to the similarity of the ionic Radii of K+ and Cs+ ,Mg+ and Co %+ and of Fe %+ and Eu %+

# ۳.۵. EFFECT OF ORGANIC COMPLEXING AGENTS

The effects of synthetic organic, chelating agents like EDTA and natural ligands such as oxalic acid on sorption of the investigated radionuclides on the natural clay minerals were studied. The results show that the synthetic and natural organic ligands studied affect the sorption of the selected radionuclides on the natural clays ( i.e. the higher the concentration of the ligand, the greater the effect in reducing the sorption)  $[\Delta_{1}\hat{r}]$ .

# \*. Desorption Of The Investigated Ions From The Loaded Clay Minerals

It was found that the maximum desorptions of the investigated radionuclides were as follows :In case of Kaolinite clay the desorption of  $Cs_1^{\psi}$  equals 1., %, 11 and 11% by washing with distilled water , EDTA and HCL , respectively .And the desorption of  $Co_7^{\phi}$ . by distilled water , EDTA and HCL equals  $1^{\Lambda}$ ,  $\Lambda^{\psi}$  and 9.%

respectively [ $^{V}$ ]. Also, the desorption of Eu\_( $1\Delta\Gamma + 1\Delta\Gamma^{e}$ ) by distilled water, EDTA and HCL equals 1%,%,  $\Gamma$ 1 and  $\Gamma\Gamma\%$ , respectively. On the other hand, in case of vermiculite clay the maximum desorption of Cs- $1\Gamma\Gamma^{e}$  equals  $1\Lambda$ , 19 and  $9\Lambda\%$  by washing with distilled water, EDTA and HCL respectively. And the desorption of  $Co_{\uparrow}$  by distilled water, EDTA and HCL are  $\uparrow \cdot$ ,  $\uparrow \Lambda$  and  $\uparrow \Lambda\%$  respectively. Also the desorption of Eu\_( $1\Delta\uparrow+1\Delta\uparrow$ ) by distilled water, EDTA and HCL equals  $1\uparrow,\lor$ ,  $\uparrow\uparrow$  and  $\uparrow\%\%$  respectively. Based on these data one can conclude that Eu $^{+}$  + ions is more fixed on Kaolinite while the desorption of vermiculite clay is higher than that of Kaolinite clay. The ion exchange mechanism may be the suggested mechanism [ $\uparrow$ ].

### ۵.Conclusion

It should be stated here that the investigations carried out in this work enabled us to collect preliminary data on some of the physicochemical characteristics of the two investigated clay minerals (Kaolinite and vermiculite). Also, they gave information about the possible interactions between some radioisotopes and the constituents of the investigated clays. From the data obtained, it can be concluded that the vermiculite clay can be used as exchanger for removal of some radioactive elements that may be present in radioactive waste solutions. Also it is recommended that the organic materials that may be present in waste solutions should be destroyed and avoided.

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