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Characterization of ion exchange resins used in the purification of the water circuits of the nuclear reactor TRIGA MARK II

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Abstract
In this work we are interested in the physical, chemical and radiological characterization of Ion Exchange Resins (IER) (MBD-15). These are polymeric beads used in the purification of nuclear reactor water circuits. The physicochemical characterization of the latter is to determine the moisture content and the adsorbed metal elements, and to study the evolution of pH and conductivity as a function of the stirring time. As for the radiological characterization involves the quantification and identification of radionuclides adsorbed by the resin. The results obtained show that the studied resin has moisture content in the vicinity of 63.07%, the presence of some metal ions such as B, Al, Fe, Si and Sb, and optionally a very low radioactivity (K40).

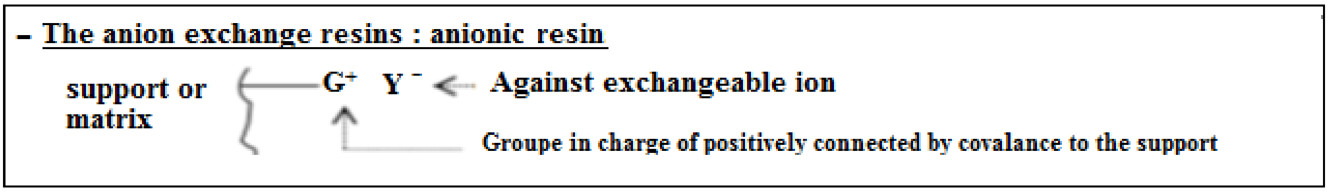
Keywords : Radioactive wastes, Radionuclide, Ion-exchange resins, Radioactivity, Nuclear reactor.

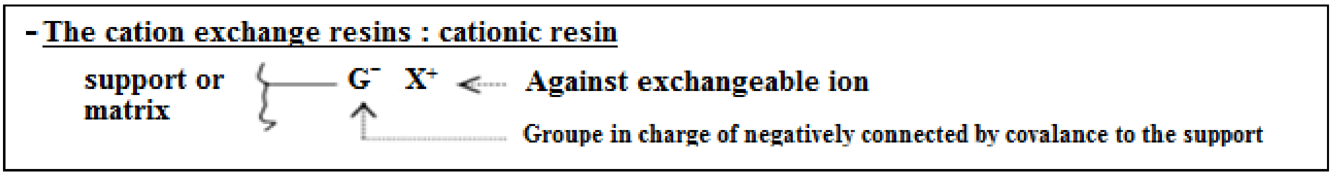
Introduction
The use of the properties of radioactivity in many sectors is responsible for the production of radioactive wastes which, for technical or economic reasons, cannot be reused or recycled. These wastes, being radioactive, have the characteristic of issuingradiation that may present risks to humans and the environment. [1] Therefore, they cannot be managed as conventional wastes and they must be supported in a specificalway. The Objective of radioactive wastes management is to handle them in a way to protect human health and the environment, now and in the future, without presenting any undue burdens on future generations [2].
In Morocco, radioactive wastes management is entrusted by the public authorities at the National Centre of Energy, Nuclear Science and Technology (CNESTEN), which set up the Nuclear Studies Centre Maâmora (CENM), a unit responsible for the collection, transportation, characterization, processing, conditioning and storage of radioactive wastes with low and intermediate level (the Radioactive Waste Operations Unit "UED"). Water circuits purification of the nuclear reactor TRIGA MARK II (rated power of 2 MW) of CENM is provided by the Ion Exchange Resins (IER) [3]. The latter play a key role in the elimination of corrosion products present at trace levels in the reactor's water circuits [4] and in the storage pools of spent fuel [5 -6 -7] (Figure 1). Thus, IER help us to ensure the safety of the personnel, control the fouling of circuits and maintain stability of the materials. After some time of using in the reactor, the saturated IER are renewed. They may be considered as radioactive wastes requiring a sensitive management for humans and the environment.The characterization is an important step in the radioactive wastes management process [8-9]. It consists in determining the physico-chemical and radiological characteristics of this solid wastes in order to establish the compliance for conditioning [10-11 -12 -13], transportation and finally its storage. [14]

2. Materials and methods
2.1 Modular system of REI
The nuclear reactor is schematically composed of the containment containing the fuel, a water supply circuit [15] in which it has, among others, a modular system containing the IER that ensures the purification of water

(1).This IER is formed by an insoluble cross-linked macromolecular functional matrix in the water, having the power to exchange its ions with metal ions and possibly the main radio-elements pollutants of water circuits of the reactor [16 -17].

We can classify ion exchange resins in two groups:





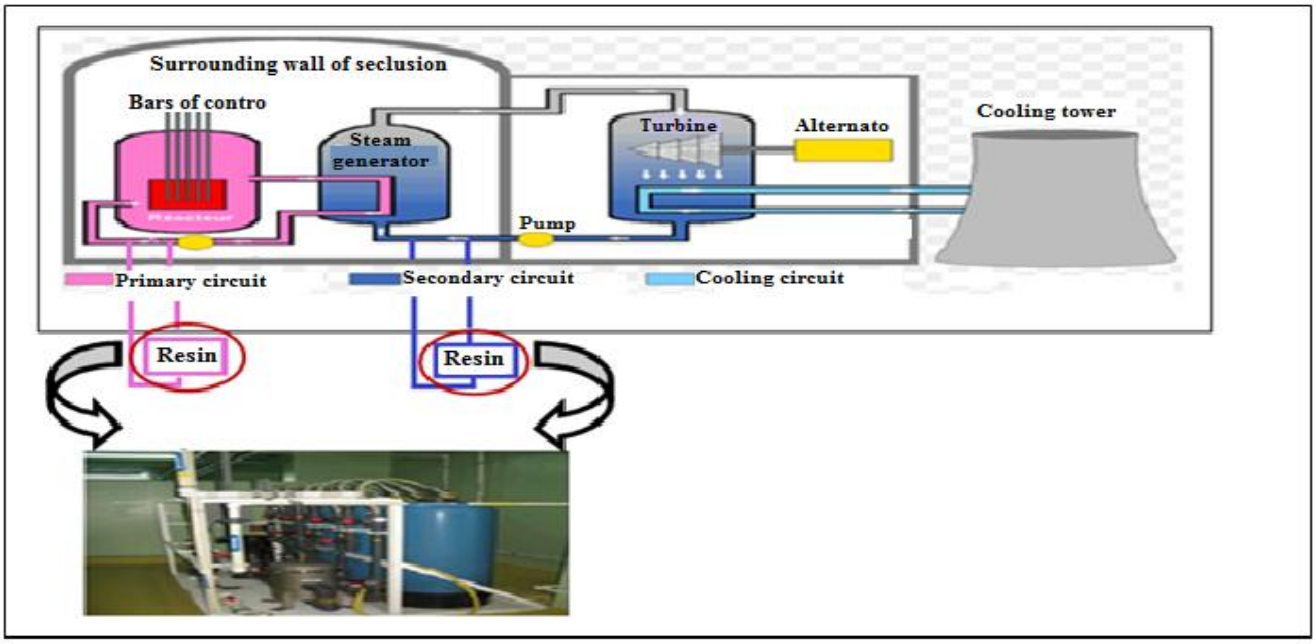


Figure 1: Modular system of IER

2.2.Characterization of IER

2.2.1. Physico-chemical characterization of IER

The physico-chemical characterization has allowed us to determine the moisture content, pH and conductivity that results and the quantification of metal elements adsorbed by the IER [18].

2.2.1.1. Rate of moisture

The retention of moisture is expressed as a percentage of the mass of a resin in its ionic shape; it is expressed by the equation below [19]:

$$\%\,\mathbf{H} = \frac{\mathbf{m1 - (m2 - m0)}}{\mathbf{m1}}\mathbf{X100}$$

- m_0 : Mass of the empty container
- m_1 : Mass of the wet IER
- m_2 : Mass of the dry IER

2.2.1.2. Evolution of the pH and the conductivity:

The evolution of the pH and the conductivity of the resin are obtained by the following procedure:

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In a series of 1 liter beakers containing volumes of 500 ml of distilled water, we introduced deferent masses of dry IER (0, 1, 2, 3, 4 and 5 g) which respectively corresponds to (blank, E1, E2, E3, E4, E5). The mixture is stirred for 80 rev / min for 24 hours in a Jar-test (Figure 2).

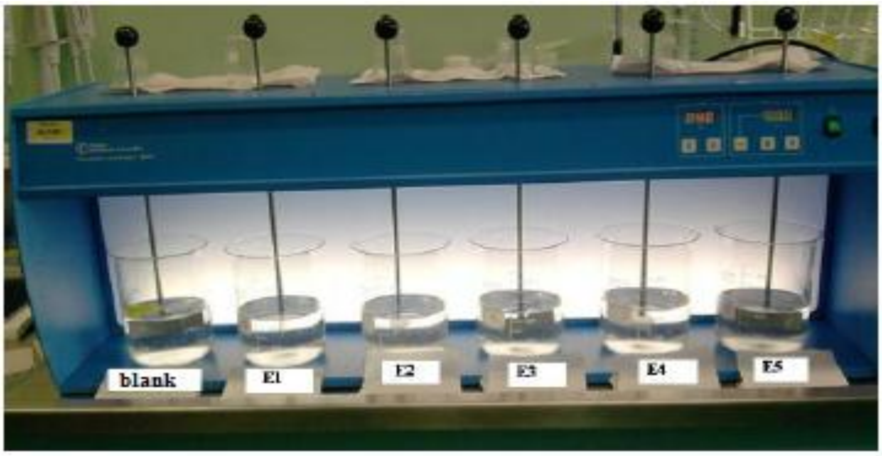

Figure 2: Jar-test

2.2.1.3. Quantification of metal elements by the ICP-MS

The Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) consists in identifying and in quantifying metal elements according to their mass [20], in the distilled water (see evolution of the pH and the conductivity), and in an acid or basic medium (release strengthened) below.

2.2.1.4. Reinforced Salting-out

To increase the release of metal elements adsorbed by IER, we performed an IER elution on a column with a solution of 0.5N HCl and by NaOH 0.5N.

2.2 Radiologic characterization:

The radiologic characterization is performed by gamma spectrometry (Figure 3). The latter consists in detecting the presence of each radionuclide and their inventories [21] in the resins studied.

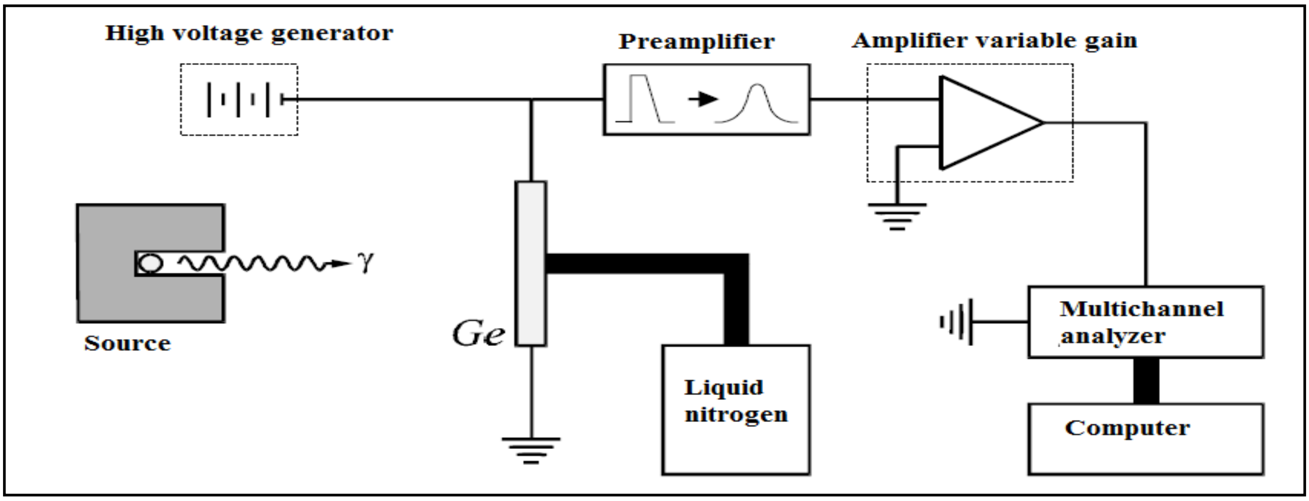

Figure 3: Gamma spectrometry device

3. Results and discussion

3.1. Physico-chemical characterization

3.1.1. Rate of moisture

The Table 1 summarizes the rate of moisture of IER for three realized essays:

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Table 1: Rate the moisture of the IER

	m_0	m_1	$(m_2\text{-}m_0)$	% H
Essay 1	1.2794	5.0012	1.7751	64.58
Essay 2	1.2797	5.0104	1.9159	61.76
Essay 3	1.2797	5.0002	1.8530	62.95
Average	1.2796	5.0039	1.8480	63.07

The rate of moisture of IER expressed in percentage has beendetermined from three essays. The calculated average is 63.07 % which explains the hydrophilicity of the ionic polymer matrix (IER).

3.1.2. Evolution of the pH and the conductivity
The figure 4 shows the evolution of the pH according to time of stirring, aqueous solutions containing quantities of IER previously dried.

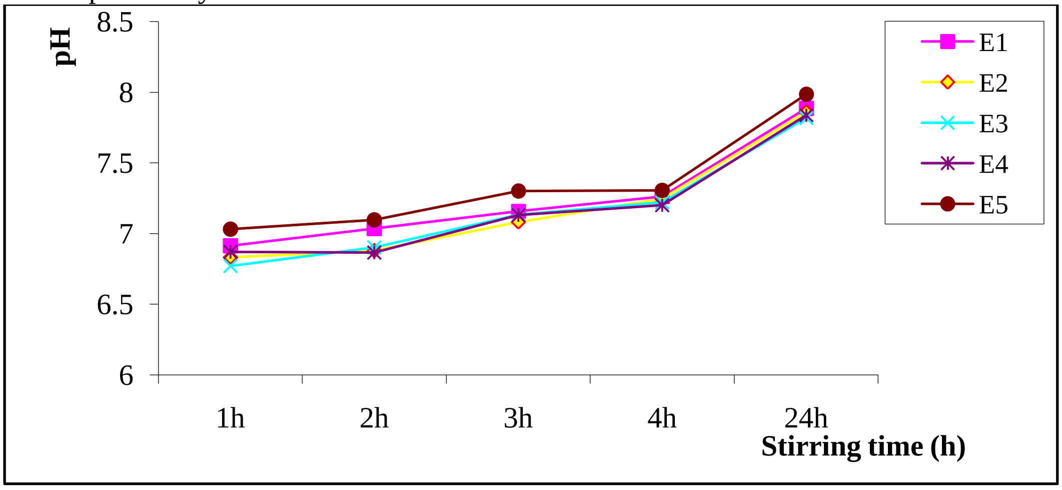

Figure 4: Evolution of the pH according to the time

We notice that the zone of the pH distributed in two phases the first one limited of pH = 6.75 and pH = 7.25 and the second bounded by pH = 7.25 and pH = 8.25. The increase in pH as a function of the stirring time is due to partial release of metal ions accentuating the basicity of the medium [22].
Figure 5 illustrates the variation of the conductivity of aqueous solutions containing dry IER compositions according to the stirring time.

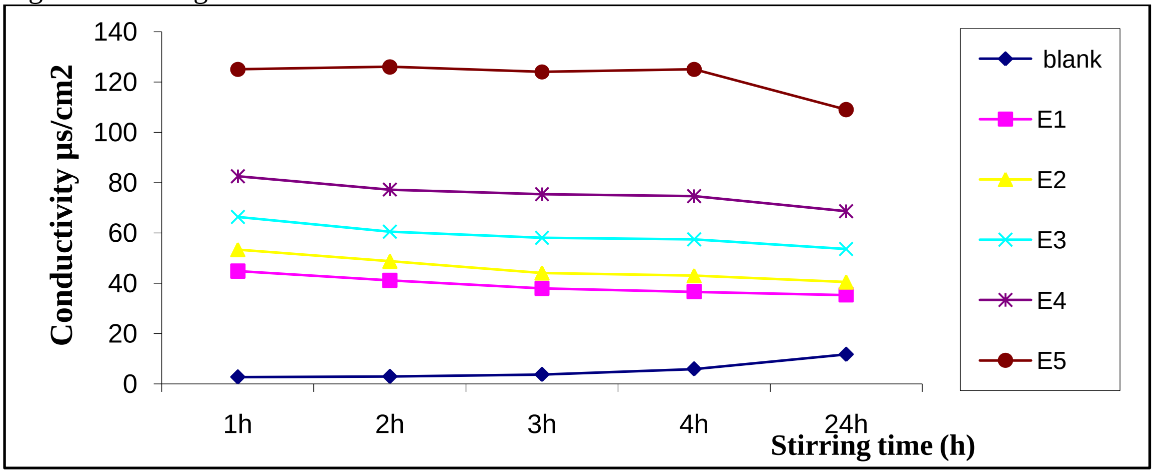

Figure 5: Evolution of the conductivity according tothe time

As for conductivity, it increases with the concentration of IER. This increase is primarily due to the metal ions relegated by IER.

3.1.3. Quantification of the metallic elements in soft conditions

The filtrates of different samples (E0, E1, E2, E3, E4, E5), used in the study of the evolution of the pH and conductivity are analyzed by the ICP-MS instrumental technique. Table 2 summarizes the mass values of different metallic elements released by the IER whose conditions are mild. In the results presented in the table above, we find the presence of elements such as K, Cr, Cu, Zn, Mo, Ag, Pb in distilled waters, and the absence in the other samples containing resin. This can only be explained by the adsorption of these elements by IER.

3.1.4. Release strengthened Ion Exchange Resins

To study elements adsorbed by ions exchange resins, we made essays of elution of the resin on a column, by a solution of HCl 0.5N and also by a solution of NaOH 0.5N.Two makes out a will of elution are made for every solution:

a) **-** Elution of the dry resin
b) **-** Elution of the wet resin

The Table 3 groups the results of this elution in the acid and basic medium

Table 2: The results obtained by the ICP-MS in the soft conditions

Nature of the elements	**Concentration of elements in each sample**					
	E0	**E1**	**E2**	**E3**	**E4**	**E5**
B (ppb)	**<3**	**333.2**	**655.8**	**908.4**	**1232**	**1597**
Na (ppm)	<1	<1	<1	<1	<1	<1
Mg (ppm)	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Al (ppb)	<30	<30	<30	<30	37.27	35.38
Si (ppm)	**<0.2**	**3.437**	**6.581**	**9.109**	**12.14**	**15.05**
P (ppm)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
K (ppm)	**0.609**	**<0.2**	**0.218**	**<0.2**	**<0.2**	**<0.2**
Ca (ppm)	<1	<1	<1	<1	<1	<1
Cr (ppb)	**3.149**	**<2**	**<2**	**<2**	**<2**	**<2**
Mn (ppb)	<10	<10	<10	<10	<10	<10
Fe (ppb)	**<10**	**29.4**	**53.54**	**29.35**	**89.86**	**137.7**
Ni (ppb)	6.776	<2	<2	<2	<2	<2
Cu (ppb)	**14.94**	**<10**	**<10**	**<10**	**<10**	**<10**
Zn (ppb)	**95.18**	**<10**	**<10**	**<10**	**<10**	**<10**
As (ppb)	<2	<2	<2	<2	<2	<2
Se (ppb)	<2	<2	<2	<2	<2	<2
Sr (ppb)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Mo (ppb)	**2.022**	**<2**	**<2**	**<2**	**<2**	**<2**
Ag (ppb)	**0.105**	**<0.1**	**0.398**	**<0.1**	**<0.1**	**<0.1**
Cd (ppb)	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Sn (ppb)	<2	<2	<2	<2	<2	<2
Sb (ppb)	<0.5	<0.5	0.618	0.785	1.007	1.4
Ba (ppb)	<10	<10	<10	<10	<10	<10
Pb (ppb)	3.777	<2	<2	<2	<2	<2
U (ppb)	3.777	3.777	3.777	3.777	3.777	3.777

Following the results presented in the Table 3, we notice that:

- The direct elution (dryResin) allowed estimating the metallic elements adsorbed by the resin compared with the results of resins previously wet with some distilled water.
- The salting-out of elements by an acid elution is more important than that of the basis.

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Table 3:Results of the analysis of the elutes

	Acid medium		Basic medium	
Parameters	**E1 (Resindries)**	**E2 (Wet resin)**	**E3 (Resindries)**	**E4 (Wet resin)**
B (ppb)	45710	15670	36490	15310
Al (ppb)	322.4	451.6	36.44	<20
Si (ppm)	58.75	46.7	52.49	42.09
P (ppb)	0.358	0.149	0.175	0.147
V (ppb)	0.897	0,676	0.494	<0.3
Cr (ppb)	63.67	4.616	2.259	<2
Mn (ppb)	8.213	<5	<5	<5
Fe (ppb)	579.3	91.89	93.97	29.6
Ni (ppb)	56.81	7.51	4.356	<3
Cu (ppb)	17.69	15.55	<10	<10
Zn (ppb)	192.9	20.2	97.28	58.67
As (ppb)	11	2.173	4.871	4.871
Se (ppb)	13.42	3.281	4.559	<2
Mo (ppb)	11.62	2.161	3.732	0.629
Ag (ppb)	0.447	2.207	2.566	4.304
Cd (ppb)	<0.2	0.511	<0.2	<0.2
Sb (ppb)	17.27	9.809	8.701	6.878
Ba (ppb)	13.3	5.801	7.216	<2
Pb (ppb)	5.906	17.15	2.706	<2

3.2. Radiological characterization

The counting for a representative sample of the IER during 1h 42 min gave the following specter (Figure 6).

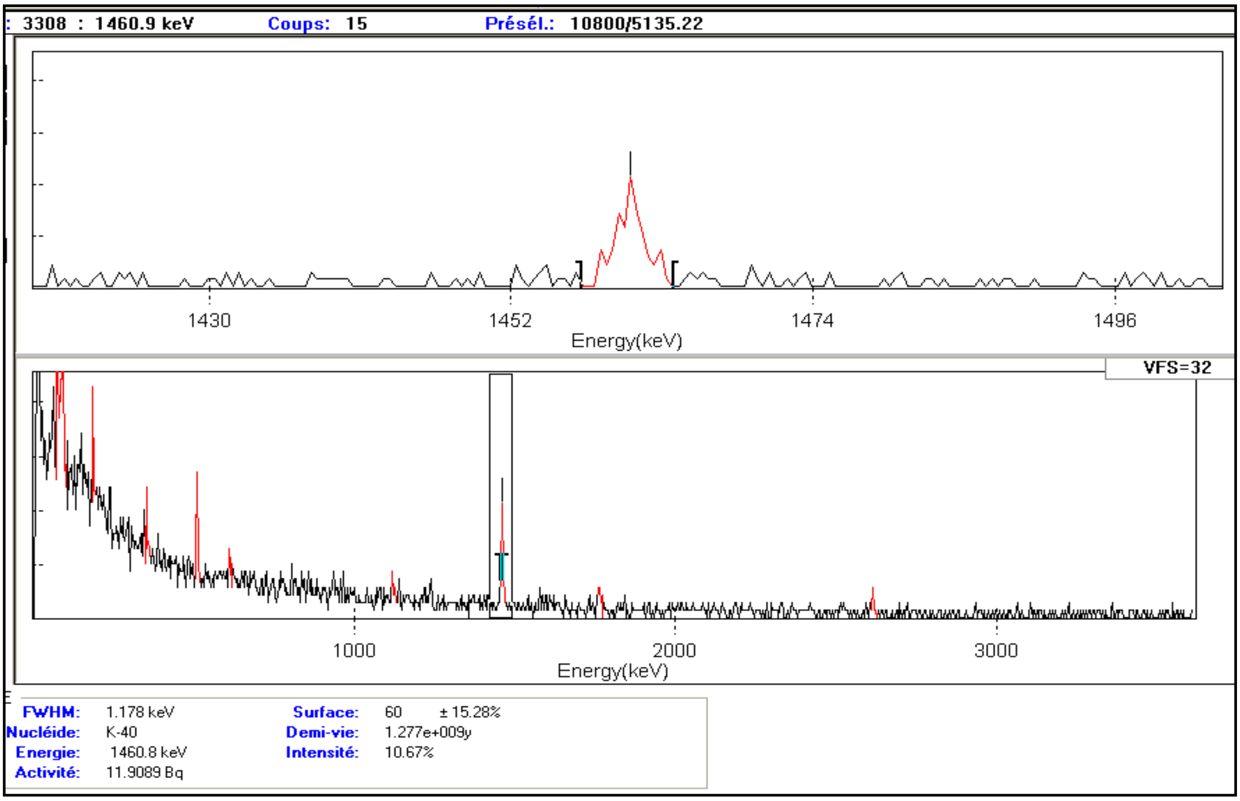

Figure 6: Spectre of IER for 1 h 42 min of counting time

The first radiological results of the obtained IER do not give enough information about radio-isotopes which represent in the IER, seeing the time reduced. In fact, we made the second counting for a representative sample of IER during 36 hours, and we obtained the following results (Table 4).

Table 4: Results of spectrometric analysis of IER for 36 hoursof counting time

Natural radionuclides		
Radioelements	**Activity (Bq/kg)**	**Limit of detection (Bq/kg)**
Chain of U-238		
Th-234	<	66.7
Ra-226	<	6.6
Pb-214	<	1.7
Chain of Th-232		
Ac-228	<	2.5
Pb-212	<	1.0
Bi-212	<	1.0
Tl-208	<	1.6
Chain of U-235		
U-235	<	3.0
K-40		
K-40	<	16.5
Artificialradioelements		
Radioelements	**Activity(Bq/kg)**	**Limit of detection (Bq/kg)**
Cs-137	<	0.5
Cs-134	<	0.4
I-131	<	0.5

The results of the analyzes of natural and artificial radionuclides such as cesium-134, cesium-137, Iodine-131, U-238 family, Th234 family (Thorium), U235 (Uranium) and K4 (potassium) on a IER sample show that the values of the activities of these radionuclides are below the measurement system of the detection limits (Table 4), which proves that this resin is a very low radioactive.

Conclusion

At the end of this study we can conclude that the IERhave a hydrophilic character which is expressed by their high moisture content (63.07%). The elution in soft and reinforced conditions allowed us to identify and quantify the adsorbed metal ions, and the results show that IER contain traces of metal ions such as B, Al, Fe, Si and Sb. Furthermore, the results of the radiological characterization showed that the resins are of a very low radioactivity.

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