**Removal of Radium from Uranium Effluent by Manganese Oxide Coated Modified Bentonite (Mn-NaB)**

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**Abstract**

The results of radiometric analysis show the presence of high level concentration of 226R (50 to 125 Bq/L) in the uranium effluent solutions waste of Gattar uranium pilot plant Eastern Desert of Egypt. These levels are higher than the maximum permissible level of 226Ra (1.1Bq/L) which needs treatment. Normally treatment consists of lime addition to increase the pH to 8 which precipitates most contaminants except 226Ra. Adsorption process provides an alternative treatment in comparison with other removal techniques. The sorption of radium (226Ra) on different adsorbent, modified bentonite (Na-B) and a mixture of modified bentonite coated by Manganese oxide (Mn-NaB) was studied. The present study focuses at the option to improve the sorption properties of bentonite via its modification and presents the possibility to remove radium cations from the uranium effluent solutions by the usage of non-homogenous bentonite coated by manganese oxides. Experimental conditions (pH, clay materials quantity to manganese oxide, contact time and associated elements ) were changed in order to determine the optimal state for adsorption of 226Ra. Column sorption of radium from uranium effluent solutions from Gattar pilot plant using (Mn-NaB) were conducted. The results showed that good adsorption capacity for radium removal in uranium influent. The capacity at breakthrough point 1.1 Bq/1 is 94.28Bq**/**g (Mn-NaB).

**Keywords:** Radium; Bentonite; Manganese Oxide; Adsorption.

**Introduction**

 226Ra presents the greatest long-term health risk due to the subsequent production of Rn gas, which causes many health troubles. According to the US EPA regulations **[1],** if Ra and 210Pb activity is < 3 pCi/g (< 0.11 Bq/g) and U activity is < 30 pCi/g (< 1.1 Bq/g), the waste can be disposed after dewatering on municipal landfills. The most of U production countries have paid a lot of attention to control U liquid industrial waste. There are at least 26 countries with large and small scale of production capabilities for U. The discharge standards of liquid effluent have some little difference.

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 For example, in Canada, the maximum allowable level of 226Ra is 0.37 Bq/1, where in China, it reaches about 1.1 Bq/1 **[2-3].** The characteristics of U liquid effluents waste depend mainly on several parameters such as: composition of the original mined ore, local climate, hydrogeological regime, geographical location and most importantly the type of mining and processing techniques used. Acidic U ores processing left behind some solid and liquid radioactive waste released into the environment causes some radiological impact on the workers. This radioactive waste contains 238U, 232Th, 226Ra together with some heavy metals which is low radioactive waste. So, public and the environment needs being treated and managed to keep our environment safe.

 With respect to 226Ra removal from U mining and milling effluent, there are different methods can be employedinclude: BaCl2 precipitation, barite adsorption and pyrolusite removal of radium **[4]**. Also, co-precipitation with BaSO4 where BaCl2 is added to co-precipitate Ra-containing highly insoluble BaSO4 sludge, followed by sedimentation and filtration. This process is successful in removing 50–95% of Ra as illustrated in the equation:

Trace Ra2+ (aq) + Excess Ba2+(aq) + 2SO42– (aq) → (Ba-Ra)SO4 (s).

 Moreover, coagulation processes with Fe or Al coagulants followed by filtration is effective in removing about 25–30% of Ra and 50–90% of U at pH 6 and 10, respectively **[5]**. Where activated sawdust, man-made zeolite, ion-exchange resin and precipitation-air aeration-hydrated Mn(OH)2 adsorption were also used to remove Ra from U effluent,**[6]**. Also, adsorption process provides an attractive alternative treatment in comparison with other removal techniques because it is more economical and readily available. Recently, hydrous manganese oxides play a major role in controlling trace metal concentration in natural water environments via adsorption and co-precipitation processes **[7-9]**. The latters have a large surface area, microporous structure, and high affinity for metal ions, providing an efficient scavenging pathway for heavy metals in toxic systems **[10]**.

Many authors used manganese dioxide and oxy-hydroxides for removing radioactive wastes via adsorption process **[11-14]**. Adsorbents in powdered form have practical limitations, including difficulty in solid/liquid separation, high head loss and leaching of the metal/metal oxide in the presence of the treated water. Table (1) summarizes some reported data which shows the usage of manganese oxide coated onto different adsorbents for removing some heavy metal ions from water.

 **Table 1.** Ions adsorption capacity by different manganese oxide coated adsorbents

|  |  |  |  |
| --- | --- | --- | --- |
| **Ions** | **Mn-coated material** | **Qmax (mg/g)** | **References** |
| **As+3** | Manganese oxide-coated-alumina | 425 | **[15]** |
| **Cd+2** | Manganese oxide modified Diatomite  | 26.6 | **[16]** |
| **Cu+2** | Manganese oxide modified Bentonite | 105.4 | **[17]** |
| **Cu+2** | Manganese oxide coated zeolite | 9.9 | **[10]** |
| **Pb+2** | Manganese oxide coated bentonite | 58.9 | **[18]** |
| **U+6** | Manganese oxide coated zeolite | 17.6 | **[19]** |
| **Cd+2** | Manganese oxide modified Bentonite | 108.6 | **[20]** |
| **Mn+2** | Manganese oxide coated zeolite | 60 | **[21]** |

It was found that, processes using manganese oxide coated media are relatively inexpensive techniques for 226Ra removal with high efficiency reached up to 80%, **[22]**. There are basically two subsequent steps illustrate the mechanism of removing 226Ra using hydrated manganese oxide (HMO) including: co-precipitation followed by contact oxidation. The following reaction summarizes the formation of hydrated manganese oxide (HMO) slurry. 2KMnO4 + 3MnSO4 + 2H2O → 5MnO2 + 4H+ + 2K+ + 3SO42–.

Firstly co-precipitation process, the water supply either containing sufficient naturally manganese or additional dissolved manganese is added. Then KMnO4 is applied to oxidize manganese to manganese dioxide prior to filtration. Manganese oxide–Ra complex forms a precipitate and is then filtered. The accumulated precipitate is periodically backwashed off the media during the normal filter backwashing. When there is insufficient manganese in the feed stream, dissolved radium will adsorb onto manganese dioxide media coating. Under this scenario, radium is not backwashed off and may accumulate in the bed. This contact oxidation technique, although effective, is generally not recommended by the Tonka Equipment Company because it carries a high potential for radium accumulation in the filter media, **[23-26]**. The adsorption mechanism for Ra using HMO is shown in the following equation:

 OH O

O = Mn + Ra2+ O = Mn Ra + 2H+

 OH O

The obtained results of radiometric analysis show that the radium content in the mineralized fractions from Gattar uranium recovery pilot plant Eastern Desert of Egypt, ranges between 16000-20000 Bq/Kg. On the other hand, it was found that 226Ra contained in the solid waste samples ranged between 8680 to 25000Bq/Kg. This study focused on the preparation of composites containing sodium bentonite and manganese oxides. The immobilization of manganese oxides on sodium bentonite surface could lead to the improvement of the bentonite sorption properties and also to overcome the limits to the use of pure manganese oxides as adsorbents.

**Experimental**

**Materials and reagents**

 The 226Ra (50 Bq mL-1 in diluted nitric acid) standard was obtained from the National Physical Laboratory **(NPL, Teddington, UK).** All other chemicals used in this study were of analytical grade and all solutions were prepared with double distilled water. On the other hand, the commercial bentonite clay sample which was kindly obtained from El Ameria Ceramic Co. Cairo, Egypt. The provided clay sample was crushed, ground and sieved to the used grain size of 0.09 mm (-200 mesh size) and chemically analyzed as represented in Table (2). Where the working liquid waste sample containing 226Ra was already provided from the Nuclear Material Authority, Gattar semi pilot plant, Egypt. Table (3) shows the chemical composition of the working liquid waste sample.

**Table (2):** Chemical composition of bentonite sample

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Constituent** | **Al2O3** | **SiO2** | **TiO2** | **Fe2O3** | **MnO** | **MgO** | **CaO** | **Na2O** | **P2O5** |
| **(Wt, %)**  | 16.6 | 56.1 | 0.98 | 8.41 | 0.04 | 3.13 | 7.96 | 5.46 | 0.17 |

**Table (3):** The composition of Gattar experimental unite effluent

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Element** | Si | Al | Fe | Mn | Na | Ca | Mg | SO4 | U | Th | Ra |
| **Conc., ppm** | 2330 | 3110 | 2080 | 210 | 135 | 95 | 170 | 1700 | 15 | 35 | 125 Bq/L |

**226Ra analysis technique**

Hyper Pure Germanium (HPGe) Detector is characterized by high resolution i.e it can discriminate between several radionuclides of adjacent similar energies. This means that it can measure the activity concentration of many radionuclides in both U and Th series in addition to 40K. The system consists mainly of a high purity germanium detector model number Gmx 60P4 and its electronic circuits.

**Preparation and characterization of 226Ra adsorbent**

A particular ground amount of natural bentonite was converted to its mono-ionic sodium form where (Na-B) was prepared from the slurry containing the activating agent (Na2CO3) and distilled water. The stabilization time was applied for 24h at ambient temperature and the final product was dried at 60°C and then mashed manually. Subsequently, the manganese oxide – NaB composite (Mn-NaB) [1/1 wt. ratio] was prepared. This adsorbent was identified using both XRD and SEM-EDAX as shown in Fig. (1, abc) and Fig. (2, ab). On the other hand, ″pure″ manganese oxide (Ref-Mn) was prepared without the addition of bentonite where manganese oxide precipitation included these steps: Potassium permanganate was dissolved in distilled water in a beaker and kept in the 90°C water bath for 15 min. Then bentonite was added into the purple solution and this suspension was mixed gently for 10 min. After that, 2M HCl were slowly added drop wise to the suspension and heated in the 90°C water bath. After that, the mixture was stirred for further 30 min. The final product was cooled at the air and washed several times using double distilled water, then dried in the oven at 100°C for 24 hours and stored **[20].** Reference sample manganese oxide (Ref-Mn) was prepared via precipitation, **[27]** as represented in the equation:

2KMnO4 + 8HCl → 2MnO2 + 2KCl + 3Cl2 + 4H2O

**Intensity [a. u.]**

**Fig. 1** X-ray diffraction (XRD) patterns of the B (a), NaB (b), and Mn-NaB (c)

**a**

**b**

**c**

**2 Theta [degree]**

** **

**b**

**a**

**Fig. 2** SEM-EDAX images of Na-B (a), Mn-NaB (b)

**Optimization of 226Ra removal process**

 Batch experiments were conducted to reflect the influence of different effective parameters to optimize the removal of 226Ra from liquid waste effluent onto the prepared adsorbent. The following parameters such as pH values of the working solution, adsorbent dose, interfering elements and the reaction time were studied at room temperature. A freshly prepared solution of NaOH and HClO4 was used to adjust the pH to the desired value in each experiment. One sample was taken before spiking with 226Ra as a background for the experiment, which was considered to be exposure time 0. Aliquots were collected continuously every 15 min and measured using liquid scintillation counting. The activity concentration of 226Ra was measured, and the percentage of removal was calculated.

It is very important to mention herein that, after the achievement of the optimum removal conditions using Mn-NaB adsorbent, the application experiments were already performed laboratory column. For this purpose a glass column of 150 mm length and 10 mm inner diameter packed with 1.00 g ± 0.0001 g of Mn-NaB adsorbent. The effluent sample with a volume of 1.5 L was poured gently into the column after adjusting its pH at (10) and the flow rate at 1.0ml/2min. The opening of the valve at the bottom of the column allowed the filtration of the sample through the bed, leading to the removal of radium and some stable elements by the Mn-NaB. The aliquots have been collected and analysed.

**Results and discussion**

**Pretreatment of the effluent liquid waste**

The working effluent liquid waste of pH 1.8 and containing considerable concentrations of Al, Si , Mn and Mg ions as shown in Table (3). This solution was firstly treated with a lime milk solution, Ca(OH)2 to precipitate the major interfering elements especially Al, Si , Mn and Mg as their hydroxide forms which eliminated by filtration. In the meantime the pH value of the filtrate free from these elements increased to pH 10-11which is very suitable for the 226Ra removal process using (Na-B and Mn-NaB) adsorbent.

**Optimization of 226Ra removal process**

**Influence of pH on the adsorption of radium**

 The effect of pH on 226Ra adsorption on two adsorbed materials (Na-B and Mn-NaB) was evaluated at pH values of 4, 6, 8, and 10. With the aim of investigating the 226Ra equilibrium for 6 h. (Fig. 3) shows 226Ra adsorption behavior onsodiumbentonite (Na-B) and manganese oxide coated sodium bentonite (Mn-NaB) at different pH values. Generally, radium adsorption increased with increasing pH and the adsorption ratios at an equilibrium state were found to be 50 % at pH 4, 75 % at pH 6 and 8, and 90 % at pH 10. The 226Ra adsorption ratio on the mixture (Mn-NaB) was about 84 % at the moderate pH values, and about 96 % in basic media (pH 10) (Fig. 3). The high adsorption capacity percent onto Na-B may be due to natrification of bentonite best enables the division of the basic montmorillonite layers which provides new space for adsorption of radium cations and leads to the increase in the overall adsorption capacity **[23].** While the higher adsorption capacity of Mn-NaB may be due to the Ra2+ ions were adsorbed onto Mn-NaB involved an ion ex-change reaction of Ra2+ with H+ on the surface and also a surface complex formation. The surface reactions of divalent ions with oxide surfaces has been described by authors **[28]**. Main interactions are summarized as:

(1) Association of the free metal ion with a surface hydroxyl group (ion-exchange with H+),

≡MnOH +‏ X2‏+  ≡MnOX‏+ ‏+ H‏

(2) Adsorption and formation of a hydrolysis complex,

 ≡ MnOH ‏ + ‏ X2‏++ H2O  ≡MnOXOH ‏ +2H‏

(3) Formation of a bidendate complex,

 2(≡ MnOH)‏ + ‏ X2‏+ (≡ MnOH )‏2 X +2H

Based on the above results, a pH value of 10 was selected for all future experiments. The equilibrium time of Ra adsorption has been determined at pH 10 for the two materials (Na-B and Mn-NaB).

**Figure (3):** pH influence on the removal of radium from uranium effluent

**Effect of Adsorbent amount on the adsorption of Ra**

The adsorption capacity and the adsorption efficiency of 226Ra at different amount of Na-B and Mn-NaB are shown in (Fig. 4). It was observed that the percentage of 226Ra adsorbed enhanced from 55% to 99% for Mn-NaB when the adsorbent amount increased from 0.5 to 2.0 g and from 0.5 to 4.0 for Na-B. It is readily understood that the number of available adsorption sites increases at high adsorbent concentration which results in an increased amount of adsorbed Ra ions. The synthetic birnessite precipitated on bentonite particles resulted in the surface charge reduction of modified bentonites. The cause of this phenomenon is the net negative layer charge of birnessite structure where Mn3+ or vacancies substitute for Mn4+ in the octahedral layers. It leads to higher radium cations interaction with the surface of MnO2 – modified bentonites (Mn-NaB) where the radium adsorption takes place on the two separated structures: the first one is, the electrostatic adsorption on basal sheets of montmorillonite structure and chemisorptions through the amphoteric ligands on edges of clay minerals **[29]**; and the second one is the ion exchange between K+ or Na+ and radium in the interlayer space of birnessite – type manganese oxide structure.

**Fig. 4** Effect of adsorbent amount on radium removal

**Interfering elements of Al, Si and Mg effect on the removal of radium**

In uranium industrial effluent, there are always some amount of aluminum, silicon and magnesium. Their contents depend on the property of the ore and process technology. The aluminum, silicon and magnesium in effluent have a great influence on the time of adsorption process to remove the radium from acidic uranium effluent. The results are shown in (Fig. 5). Because the aluminum, silicon and magnesium contents in effluent are relatively high, the results of removal of radium by Na-B and Mn-NaB adsorption are poor and cannot meet the requirements at these high impurity levels. As in shown in (Fig. 5) when the concentration of Si, Al and Mg up to 450 ppm the adsorption decreases to 75, 55 and 67% respectively. So two steps are needed to process the effluent. First effluent pH is adjusted to 8 by lime milk, and Al, Si and Mg are formed and removed. The second step is taking the supernatant liquid to pH 10 then contact with Mn-NaB to remove radium by adsorption.

**Contact time influence on the radium adsorption**

**Fig. 5** Interfering elements influence on the removal of radium efficiency at pH 1.8

To study the effect of contact time upon radium adsorption on Na-B and Mn-NaB a series of adsorption experiments was performed at pH 10. A quick increase in Ra adsorption ratio with time was observed, the obtained results were plotted in (Fig. 6). From this figure, the radium adsorption efficiency attained about 45 and 52 % for Na-B and Mn-NaB respectively at the first experiment (of 30 min). Radium efficiencies steadily increased by increasing time till the experimental 180 min 84 and 97 % for Na-B and Mn-NaB respectively. For increasing the contact time above 180 minutes gave no any improvement in the adsorption efficiency by Mn-NaB but improvement the adsorption capacity for Na-B to 90%. Therefore, 180 min is the optimum contact time for Mn-NaB while 240 minutes is the optimum time for radium adsorption onto Na-B.

**Fig. 6** Effect of contact time on radium removal from uranium effluent at pH 10

**Column Application of Mn-NaB adsorbent**

Because the aluminum, silicon and magnesium contents in this effluent are relatively high, the results of direct removal of 226Ra by Mn-NaB adsorption are poor and cannot meet the requirements at these high impurity levels. So two steps are needed to process the effluent. First effluent pH is adjusted to 8-10 by lime milk, and Al Si and Mg are formed and removed as shown in Table (4). The second step is taking the supernatant liquid to pH 10 then contact with Mn-NaB to remove radium through column adsorption.

In about two days operation, 1500 mL uranium effluent was processed after Si, Al and Mg removal at pH 8.0 and a flow rate of 1 mL/2min. Inlet pH of the effluent was about 10, 226Ra was about 100 Bq/L as show in Table (5) and (Fig. 7) about 1400 mL of the discharged uranium effluent had 226Ra content below 0.3 Bq/L and a total of 94.28 Bq/g 226Ra was adsorbed by 1.0 gram of manages oxide coated bentonite (Mn-NaB) at breakthrough point 1.1 Bq/L. In general, as the experiments above show, pH has a great influence on the adsorption of 226Ra by manages oxide coated bentonite (Mn-NaB). At the adsorption pH (10) of the effluent, manages oxide coated bentonite (Mn-NaB) shows good adsorption capacity for 226Ra removal in uranium influent. The capacity at breakthrough point (the industrial discharge standard of 226Ra in effluent, 1.1 Bq/L) is 94.28 Bq**/**g (Mn-NaB) while the total capacity is 127.28 Bq**/**g (Mn-NaB).

**Table 4.** The composition of Gattar experimental unite effluent at pH 2 and 10

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Element** | **Si** | **Al** | **Fe+3** | **Mn** | **Na** | **Ca** | **Mg** | **U** | **Th** | **Ra** | **pH** |
| **Conc., ppm** | 2330 | 3110 | 2080 | 210 | 135 | 95 | 170 | 15 | 35 | 125 Bq/L | 2.0 |
| **Conc., ppm** | 116 | 60 | 230 | 150 | - | - | 55 | 4 | 29 | 100 Bq/L | 10.0 |

**Fig. 7** Break through profile for radium adsorption onto Mn-Na B

**Table (5):** Column adsorption radium results by Mn-NaB

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **No** | **Outlet volume, mL** | **pH of outlet effluent** | **Total volume, mL** | **Ra content in outlet****effluent, Bq/L** | **Ra adsorbed on Mn-NaB** |
| 1 | 50 | 9.8 | 50 | 0.15 | 4.85 |
| 2 | 50 | 9.9 | 100 | 0.1 | 4.90 |
| 3 | 50 | 10 | 150 | 0.08 | 4.92 |
| 4 | 55 | 10 | 205 | 0.09 | 4.91 |
| 5 | 50 | 10.1 | 255 | 0.07 | 4.93 |
| 6 | 50 | 10.2 | 305 | 0.08 | 4.92 |
| 7 | 45 | 10 | 350 | 0.09 | 4.91 |
| 8 | 55 | 10.1 | 405 | 0.1 | 4.90 |
| 9 | 50 | 10.1 | 455 | 0.12 | 4.88 |
| 10 | 55 | 10 | 510 | 0.15 | 4.85 |
| 11 | 45 | 9.9 | 555 | 0.18 | 4.82 |
| 12 | 50 | 9.8 | 605 | 0.21 | 4.79 |
| 13 | 50 | 9.8 | 655 | 0.28 | 4.72 |
| 14 | 50 | 9.9 | 705 | 0.34 | 4.66 |
| 15 | 45 | 10 | 750 | 0.4 | 4.6 |
| 16 | 50 | 10.2 | 800 | 0.42 | 4.58 |
| 17 | 50 | 10.1 | 850 | 0.45 | 4.55 |
| 18 | 50 | 9.9 | 900 | 0.56 | 4.44 |
| 19 | 50 | 9.9 | 950 | 0.9 | 4.10 |
| 20 | 50 | 10 | 1000 | 1.1 | 3.9 |
| 21 | 50 | 10.1 | 1050 | 1.5 | 3.5 |
| 22 | 100 | 10.2 | 1100 | 2.2 | 2.8 |
| 23 | 100 | 10.2 | 1200 | 3.5 | 1.5 |
| 24 | 100 | 10.1 | 1300 | 4.7 | 0.3 |
| 25 | 100 | 10.1 | 1400 | 5.1 | 0.00 |

 **Conclusions and Recommendations for Future Work**

Manganese oxide coated modified bentonite (Mn-NaB) is an effective adsorbent for radium removal from uranium effluent resulting during uranium milling processes. Two steps are needed to process the effluent. First step effluent pH is adjusted between 8-10 by lime milk while Al, Si and Mg are formed and removed. The second step is taking the supernatant liquid to pH 10 then contact with Mn-NaB to remove radium through column adsorption. The capacity at breakthrough point (the industrial discharge standard of 226Ra in effluent, 1.1 Bq/L) is 94.13 Bq**/**g (Mn-NaB) while the total capacity is 127.28 Bq**/**g (Mn-NaB). This study strongly recommends the use of manganese oxide coated bentonite (Mn-NaB) to remove radioactive wastes; especially radium such wastes arise from technologies producing uranium. The most difficult problem in these experiments was the permeability of solutions through the column. Therefore, there is a need to improve the permeability of Mn-NaB. We recommends the chosen amount of the mixture of Mn-NaB with the sand to increase the permeability.

**References**

[1] U.S. Environmental Protection Agency. Office of Drinking Water. Suggested Guidelines for Disposal of Drinking Water Treatment Wastes Containing Naturally Occurring Radionuclides. July, 1990.

[2] N.W. Schidtke, D. Averill and D.N. Bryan, “Remove of 226Ra fromtailings pond. Proceedings of the seminar on management, stabilisation and environmental impact of uranium mill tailings”, Albuquerque, USA, July, (1978).

[3] S. Cheng, J. LIU and K. YU, “Treatment of wastewater in tailings dam of a uranium mill by lime precipitation-air aeration”, Uranium mining & Metallurgy, 2(2), p. 52, (1983).

[4] J. Environment protection article (1), Environmental Office. Metallurgy industry, (1977).

[5] K.L. Martins and A.G. Myers, Controlling radionuclides in water treatment plants: removal, disposal, and exposure minimization. In Proc. of the AWWA Water Quality Technology Conference. New York, PP. 1077–1109, (1993).

[6] J.W. Jl, “Treatment of effluent from uranium mining. Remove the uranium and radium”,

 Nuclear energy publisher, (1982).

[7] H.S. Posselt, F.J. Anderson and W.J. Weber, “Cation sorption on colloidal hydrous manganese dioxide”, Environmental Science & Technology 2 (12), PP. 1087–1093, (1968). DOI: 10.1021/es60023a005

[8] R.M. Mckenzie, “Proton release during adsorption of heavy metals ions by a hydrous manganese dioxide”, Geochimica et Cosmochimica Acta 43, PP.1855–1857, (1979).

 https://doi.org/10.1016/0016-7037(79)90034-6

[9] L.S. Balistrieri and J.W. Murray, “The surface chemistry of δMnO2 in major ion sea water” Geochimica et Cosmochimica Acta, 46, PP.1041–1052, (1982).

 https://doi.org/10.1016/0016-7037(82)90057-6

[10] W. Zou, R. Han, Z. Chen, J. Shi and Liu, “Characterization and properties of manganese oxide coated zeolite as adsorbent for removal of copper(II) and lead(II) Ions from solution”, Journal of Chemical & Engineering Data, 51, PP. 534–541, (2006).

 DOI: 10.1021/je0504008

[11] J.G. Catts and D. Langmuir, “Adsorption of Cu, Pb, and Zn by dMnO2: applicability of the side binding-surface complexation model”, Applied Geochemical, 1, PP. 255– 264, (1986). https://doi.org/10.1016/0883-2927(86)90010-7

[12] G. Fu, H.E. Allen and C.E. Cowan, “Adsorption of cadmium and copper by manganese oxide”, Soil Science, 152, PP. 72–81, (1991).

[13] H. Tamura, N. Katayama and R. Furrich, “The Co2+ adsorption properties of Al2O3, Fe2O3, Fe3O4, TiO2, and MnO2 evaluated by modeling with the Frumkin isotherm”, Journal of Colloid Interface Science, 195, PP. 192–202, (1997).

 https://doi.org/10.1006/jcis.1997.5148

[14] A. Birsen and A.D. Timothy, “Application of MnO2 coated scintillating and extractive scintillating resins to screening for radioactivity in groundwater”, Nuclear Instruments and Methods in Physics Research Section A, 505, PP. 458–461, (2003).

 https://doi.org/10.1016/S0168-9002(03)01120-3

[15] S.M. Maliyekkal, L. Philip and T. Pradeep, “As(III) removal from drinking water using manganese oxide-coated-alumina: performance evaluation and mechanistic details of surface binding”, Chemical Engineering Journal, 153 (1– 3), PP.101–107, (2009).

 https://doi.org/10.1016/j.cej.2009.06.026

[16] Y. S. Al-degs , M. F. Tutunju and R. A. Shawabkeh , “The feasibility of using diatomite and Mn diatomite for remediation of Pb2+, Cu2+, and Cd2+ from water”, Separation Science and Technology, 35, PP. 2299–2310, (2000).

 https://doi.org/10.1081/SS-100102103

[17] E. Eren, “Removal of copper ions by modified Unye clay, Turkey”, Journal of Hazardous Materials, 159, PP. 235–244, (2008). https://doi.org/10.1016/j.jhazmat.2008.02.035

[18] E. Eren, B. Afsin and Y. Onal, “Removal of lead ions by acid activated and manganese oxide-coated bentonite”, Journal of Hazardous Materials, 161, PP. 677– 685, (2009).

 https://doi.org/10.1016/j.jhazmat.2008.04.020

[19] R. Han, W. Zou, Y. Wang and L. Zhu, L., “Removal of uranium(VI) from aqueous solutions by manganese oxide coated zeolite: discussion of adsorption isotherms and pH effect”, Journal of Environmental Radioactivity, 93, PP. 127–143, (2007).

 https://doi.org/10.1016/j.jenvrad.2006.12.003

[20] S. Tomas, D. Silvia and M. Annamaria, “Characterization of Bentonite Modified by Manganese Oxides”, Universal Journal of Geoscience, 1(2), PP. 114-119, (2013).

 DOI: 10.13189/ujg.2013.010211

[21] R. T. Silvio and R. Jorge, “Removal of Mn2+ from aqueous solution by manganese oxide coated zeolite”, Minerals Engineering, 23, PP. 1131–1138, (2010).

 https://doi.org/10.1016/j.mineng.2010.07.007

 [22] L.B. William, R.J. Schliekelman, L.B. Dorothy, R.B. Charles and M.M. Ira, “Radium removal efficiencies in water treatment processes’, Journal (American Water Works Association), 70 (1), pp. 31-35, (1978). http://www.jstor.org/stable/41269311

[23] <http://www.mnawwa.org/about/councils/training/research/> radionuclidesremoval.pdf (accessed 08.12.2011).

[24] Radium Removal from Potable Water. Tonka Technical Bulletin. Tonka Equipment Company, Plymouth, Minnesota, USA, (2010).

[25] www.stuk.fi/julkaisut/stuk-a/stuk-a169.html (accessed 08.12.2011).

[26] R.L. Valentine, R.C. Splinter, T.S. Mulholland, J.M. Baker, T.M. Nogaj and J. Horng, Project Summary: A Study of Possible Economical Ways of Removing Radium from Drinking Water: EPA/600/S2-88/009. US EPA, Washington, April (1988).

[27] W. Cole, A. Wadsley and A. Walkley, “An X‐Ray Diffraction Study of Manganese Dioxide”, Journal of the Electrochemical Society, 92 (1), PP. 133-158, (1947).

 DOI: 10.1149/1.3071811

[28] R. Han, W. Zou, Z. Zhang, J. Shi and J. Yang, “Removal of copper(II) and lead(II) from aqueous solution by manganese oxide coated sand I. Characterization and kinetic study”, Journal of Hazardous Materials B, 137, PP. 384–395, (2006).

 DOI: 10.1016/j.jhazmat.2006.02.021

[29] J. Makovnikova, G. Barancikova, P. Dlapa and K. Dercova, “Inorganic contaminants in soil ecosystem”, Chemické listy, 100 (6), PP. 424-432, (2006).