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DYNAMIC STUDIES ON SORPTION CHARACTERISTICS OF ^{226}Ra ON MANGANESE DIOXIDE

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Characteristics of ^{226}Ra sorption on MnO_2 were investigated by dynamic tests using different types of water under various conditions, such as ^{226}Ra activity, pH, chemical species and contact time. Tests indicate that sorption varies with different column geometries and contact times. Sorption values of 23% to 92% were obtained with 10.00g of MnO_2 at flow rates of 1100mL min^{-1} to 16mL min^{-1} respectively, using column heights of 16mm to 65mm and internal diameters of 19.0mm to 9.25mm respectively. The sorption amount showed no dependence on ^{226}Ra activity (upto 1000Bq), types of water (distilled, tap and simulated groundwater) and pH when this exceeds 3.6 (pH at zero point charge of MnO_2 is 5.5). An enthalpy change value of 20.0 kJ mol^{-1} was obtained indicating a chemical and/or specific sorption mechanism(s).

In recent years much interest has been focussed on the possible impact of naturally occurring radionuclides on man. Of the many radionuclides found in nature, ^{226}Ra is considered very important because it is frequently found in environmental waters and it is a bone seeking radioisotope. In view of possible hazards and concerns, it would be desirable to establish a quick and efficient method for preconcentrating ^{226}Ra from environmental waters prior to analysis. It is well known that oxides of iron and manganese are scavengers of a wide range of elements and have more rapid kinetics of sorption than most oxides [1,2]. Manganese dioxide (MnO_2) has been known to be the stronger sorber of radium[2,3-5] and the most stable oxide for reliable sorption under most conditions as compared to other oxides[4,6]. For example, MnO_2 is 40 times a better sorber than ferric hydroxide for radium sorption[7-9]. In this study, the two main methods for studying sorption involve static (batch) and dynamic (column) tests. The static method utilizes a suspension of sorbent (MnO_2) in the solution which has been spiked with a radionuclide (^{226}Ra). Continuous agitation of the suspension is maintained during the reaction period prior to sampling analysis. Most sorption studies of radium onto MnO_2 under various conditions have been performed by batch tests[5,7,11-13]. Dynamic methods utilize a spiked solution passing through a column of sorbent. This has the advantage of passing large volumes of water through the sorbent providing preconcentration of radionuclides in a relatively short period of time. All dynamic studies of ^{226}Ra sorption on MnO_2 have used columns containing acrylic fibres coated with fine particles of MnO_2 for removal of ^{226}Ra from environmental water[1,3,7-9,14-23]. No study has been found which focuses on the behaviour of ^{226}Ra sorption on MnO_2 using dynamic tests under a variety of conditions. In this study, characteristics of ^{226}Ra sorption on MnO_2 will be investigated using different types of water (i.e. distilled, tap and simulated ground waters) under various conditions, such as ^{226}Ra activity, pH, chemical species, flow rate and contact time (i.e. the time spent by the solution in contact within the MnO_2 medium). In the case for batch tests, the contact time represents the total mixing time between the two phases while in column tests, the contact time represents the period that an arbitrarily small volume of the solution is in contact with the MnO_2 medium. Sorption measurements were carried out using manganese dioxide (MnO_2) material of particle size within 0.60 - 1.20mm.

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Experimental

X-ray diffraction (XRD) analysis: The MnO_2 was structurally examined by XRD, using a Philips X-ray diffractometer (PW-1050). A typical XRD pattern is shown in Fig. 1. The XRD pattern reveals diffuse peaks indicative of a disordered structure. The pattern that it mostly complies with is that of γ/ε MnO_2.

Fourier-Transform Infrared (FT-IR) spectrometry : FT-IR spectrum of MnO_2 was measured in the range of 500-5000 cm^{-1} using a Perkin-Elmer 2000 FT-IR connected to a FT-IR microscope. A sample spectrum is shown in Fig. 2. Small broad peaks were obtained in the range of 3600-3800 cm^{-1} as a result of hydroxyl groups from atmospheric water, and a

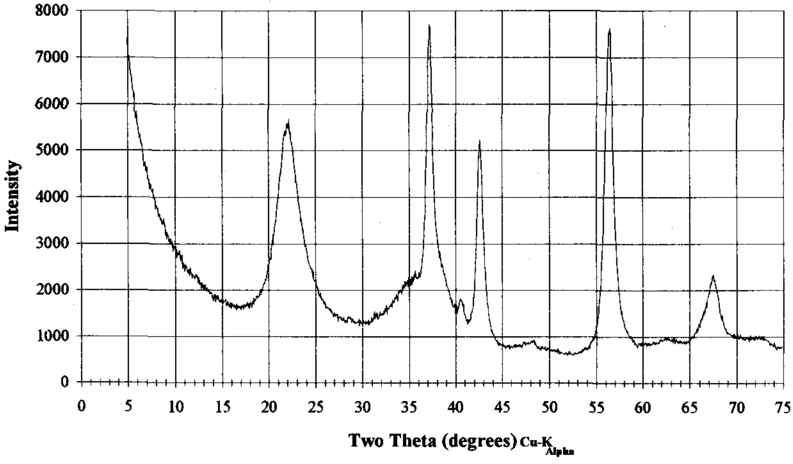

Fig. 1 XRD pattern of MnO_2

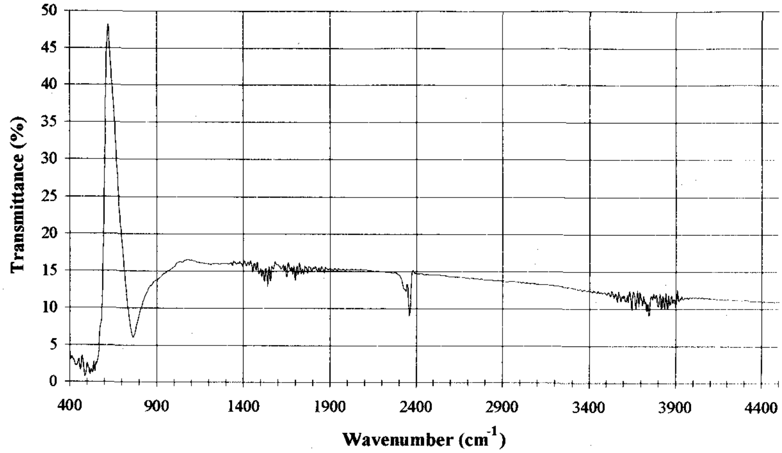

Fig. 2 FTIR spectrum of MnO_2

band at 1600 cm^{-1} resulting from the bending vibration of water molecules. These peaks indicates that MnO_2 contains atmospheric water as the major component and shows no indication of the presence of interstitial water. The main bands were obtained at approximately 500-650 cm^{-1} as a result of Mn-O vibrations.

Sorption measurements: Initial batch tests were carried out using ^{226}Ra under various contact times and temperatures. All reagents used were of analytical grade and carrier-free ^{226}Ra in 0.5M HCl solution (specific activity ca. 44.68 kBq g^{-1} ± 3.7%, 5.0392 g) obtained from Amersham International. The standard was diluted to obtain a working standard solution with a specific activity of 252 Bq g^{-1} ± 3.7%. The sorption studies were performed by equilibrating 10.00g of MnO_2 with 20.0 mL of solution containing known activity of ^{226}Ra (≈260Bq). The pH of the solution was maintained at 10.0 using a bicarbonate/carbonate buffer. The mixture was kept in perspex (methyl methacrylate) containers and were agitated in a temperature-controlled water-bath/agitator for various contact times and temperatures. The mixture was filtered for phase separation and the MnO_2 was analysed for ^{226}Ra activity by measuring the 186 keV γ-emission using a closed-end coaxial germanium well detector (Canberra - GCW2523). The experimental procedures for the measurements of the sorption amount and distribution coefficient (K_D) are described elsewhere[24]. Counting efficiencies were obtained by using a standard pitchblende ore obtained from the Department of Energy, Idaho Operations Office, USA. The efficiencies obtained were comparable with those obtained by measuring a dried mixture of ^{226}Ra standard solution in MnO_2.

Column Tests: Sorption measurements of ^{226}Ra on MnO_2 using column tests were investigated using different types of water under various conditions, such as ^{226}Ra activity, pH, chemical species and contact time. These results will be used to investigate the parameters that influence the sorption process and hence obtain a quantitative measure on the kinetics of the sorption process. The apparatus is comprised of a polypropylene column, packed with a constant mass of MnO_2 (10.00g). A modified tap is connected to the outlet while a polypropylene influent vessel is connected to the inlet of the column. A spiked ^{226}Ra water solution is poured into the vessel via the inlet. A marinelli beaker which acts as the effluent vessel is placed on a top loading balance. The water solution interacts with the MnO_2 medium in a vessel of a given height and internal diameter and the effluent is collected in the marinelli beaker. Pressurised air is used to force the water through the column, while an inlet tap acts as a pressure control regulator so consistent flow rates are obtained. The apparatus may be crude, but it gave constant flow rates as verified by the linear plots of volume (or mass) of water collected versus time. At the end of the experiment, the marinelli beaker is placed on top of a high purity germanium (HPGe) coaxial (Gamma-X) (EG&G Ortec-GMX 25280-J) detector where the ^{226}Ra activity of the effluent is determined. The MnO_2 material is placed in a specially prepared polypropylene sample container and placed in a HPGe well detector so the ^{226}Ra activity is determined and the sorption amount is evaluated.

Results and Discussion

Batch Tests: The results of this experiment involving sorption uptake as a function of contact time is shown in Fig. 3.

From Fig. 3, the time-growth of sorption of Ra^{2+} ions on MnO_2 is rapid as 42% sorption was obtained at 0.25 hours and an apparent equilibrium between the two phases is established at approximately 15 hours. Initially, the sorption is rapid since there are unoccupied vacancies/sites, while at a later stage, the sorption is much slower since the vacancies/sites have been occupied thus providing fewer vacancies/sites. This leads to a plateau region,

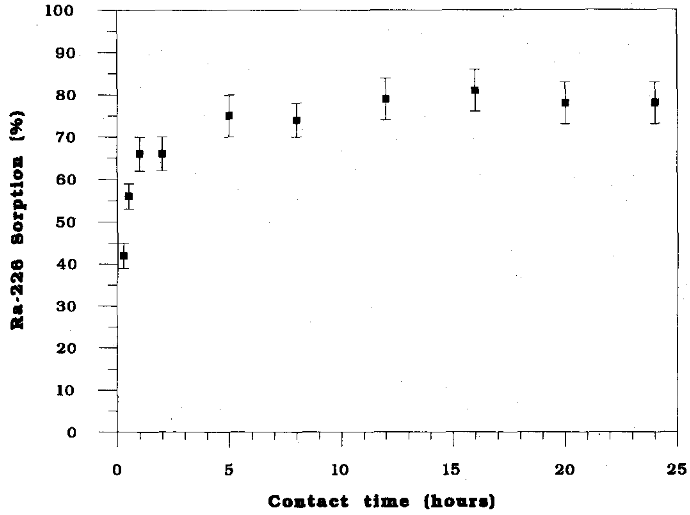

Fig.3 Contact time variation with sorption of ^{226}Ra on MnO_2. Initial activity of ^{226}Ra: 260 Bq. Temperature: 293 °K. pH: 10.0.

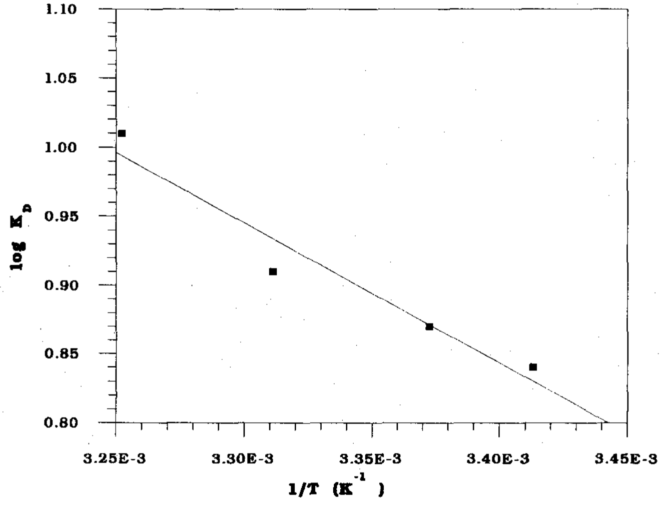

Fig. 4 Log K_D vs 1/T for ^{226}Ra on MnO_2

where an apparent equilibrium state between the two phases for a particular ^{226}Ra activity (amount of Ra^{2+} ions) in the sorbate is reached. This concept was also suggested by others who investigated the sorption of Ba^{2+} (chemical analog of Ra^{2+}) on hydrous manganese dioxide[25]. They have indicated that equilibrium is reached between the two phases in 30 minutes. In our system, apparent equilibrium is reached at ≈15 hours. One possible explanation is that the agitation process may partly influence the equilibrium process. The agitation process used involved a constant back and forth movement in the horizontal direction. The results of this experiment involving sorption uptake as a function of temperature is shown in Fig. 4 indicating the sorption of ^{226}Ra on MnO$_2$ increases with increasing temperature. Unfortunately a larger temperature range could not be obtained due enhanced mechanical breakdown of the MnO$_2$ at higher temperatures. The distribution coefficient at equilibrium increases from 6.92 -10.33 mL g^{-1} with an increase in temperature of the system from 293.0 - 307.5 °K. This increase in sorption with temperature confirms the process to be endothermic in nature and can be explained by an acceleration in the kinetic sorption process. Similar results have been obtained in the study of Ba^{2+} sorption on hydrous manganese oxide[25]. The enthalpy change has been found to be 20.0 kJ mol^{-1} (cf. Fig. 5) using the Clausius-Clapeyron formula, which is significantly higher than the enthalpy change for ion-exchange (electrostatic) or physical sorption (8.4 - 12.6 kJ mol^{-1})[25]. This suggests the sorption process does not proceed via an ion-exchange process thus presumably indicating a specific and/or chemical sorption process. This is further supported by other authors[25] who have obtained a smaller enthalpy change value of 14.9 kJ mol^{-1} for the chemisorption of Ba^{2+} ions on hydrous manganese oxide.

Column Tests - Sorption behaviour of ^{226}Ra on MnO$_2$ as a function of ^{226}Ra activity: Preliminary experiments were performed by gravity feeding distilled water spiked with ^{226}Ra at different activities through MnO$_2$ at a constant flow rate. Tests were also performed with different masses of MnO$_2$ in the column. The solution was maintained at a constant pH of 10.0 by means of a bicarbonate/carbonate buffer. The results of this experiment are shown in Figs. 5 and 6.

From Fig. 5, the ^{226}Ra activity in the MnO$_2$ is sorbed linearly with ^{226}Ra activities upto 1000 Bq used in the feed solution. This indicates that the MnO$_2$ material has sufficient sites/vacancies so that no saturation occurs. From Fig. 6, the percentage sorption of ^{226}Ra is found to be constant within in each mass of MnO$_2$ for all ^{226}Ra activities used in the feed

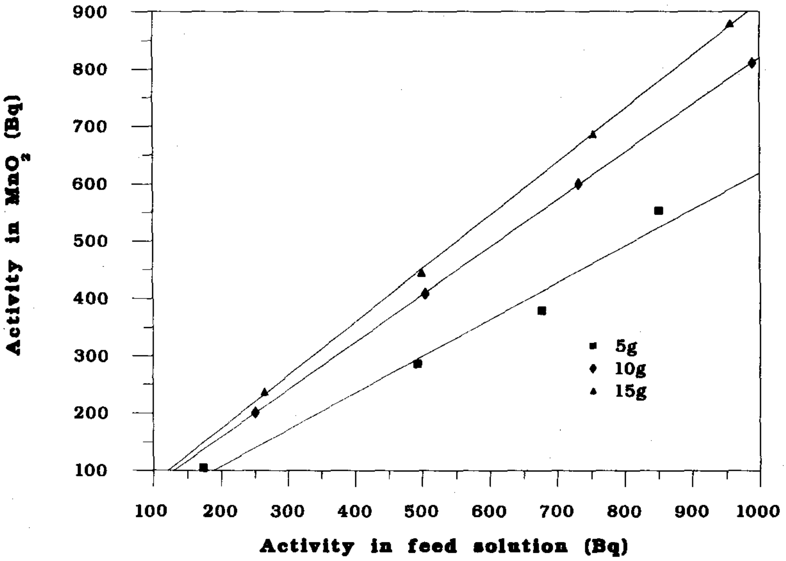

Fig. 5 ^{226}Ra on MnO$_2$ as a function of ^{226}Ra activity and mass of MnO$_2$. pH: 10.0. Flow rate: 55 ml min^{-1}

solution for constant pH and flow rate. The plot for 15 g shows a larger percentage sorption uptake compared with the other lower masses. It is also evident from Fig. 6 that the sorption is independent of the activity of the feed solution. Since the masses used occupy different heights within the column, the contact time of the solution will be longer for the 15 g MnO_2 column than the 5 g and 10 g MnO_2 columns, consequently the plot for the 15 g will show greater sorption.

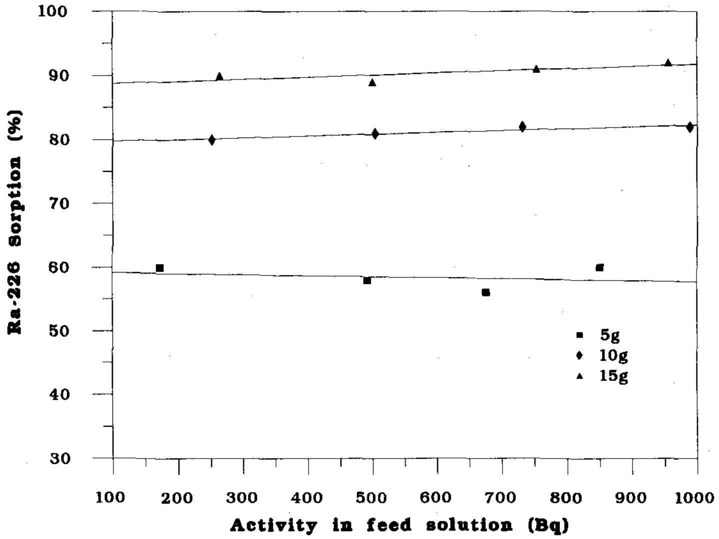

Fig. 6 ^{226}Ra sorption as a function of ^{226}Ra activity and mass of MnO_2. pH:10.0. Flow rate:55 mL min^{-1}

Sorption behaviour of ^{226}Ra on MnO_2 as a function of pH and chemical species: Since pH of solutions can alter the surface charge of metal oxides/hydroxides, it is important to examine sorption of ^{226}Ra on MnO_2 as a function of pH. Usually sodium hydroxide (NaOH) and hydrochloric acid (HCl) reagents are used in altering the pH of the solution. Since the pH of a solution can be altered by different chemical species as evidenced in environmental waters, tests were carried out using NaOH and sodium carbonate (Na_2CO_3) as well as HCl solutions in adjusting the pH of ^{226}Ra spiked distilled water solution. The results from the experiment are shown in Fig. 7. From Fig. 7, the sorption of ^{226}Ra on MnO_2 is at a plateau over a wide range (pH $\geq$ 3.6 - 12.0) and tends to decrease dramatically at pH values below about 3.6. The use of different chemical species (i.e. NaOH and Na_2CO_3) in the solution had no effect on the percentage sorption uptake. A similar trend was found by other works[25] for the adsorption of Ba^{2+} ions on hydrous manganese oxide. Gamma-MnO_2 was noted in having a pH of zero point charge (zpc) of approximately 5.5[16], thus below a pH of about 5.5, the charge on the surface of the MnO_2 will remain positive. Since the plateau region extends below a pH of 5.5, it is believed that ion-exchange is not the main sorption process. This is further supported by the batch tests which yielded an enthalpy change value of 20.0 kJ mol^{-1}, significantly higher than ion exchange or physical sorption process (8.4-12.6 kJ mol^{-1})[25]. Other authors[13,14] have shown the ^{226}Ra adsorption efficiency on δ-MnO_2 to be constant over a pH range of 2-10. A possible explanation is δ-MnO_2 has a zpc of 1.3 - 2.8[2,3,26]. So the

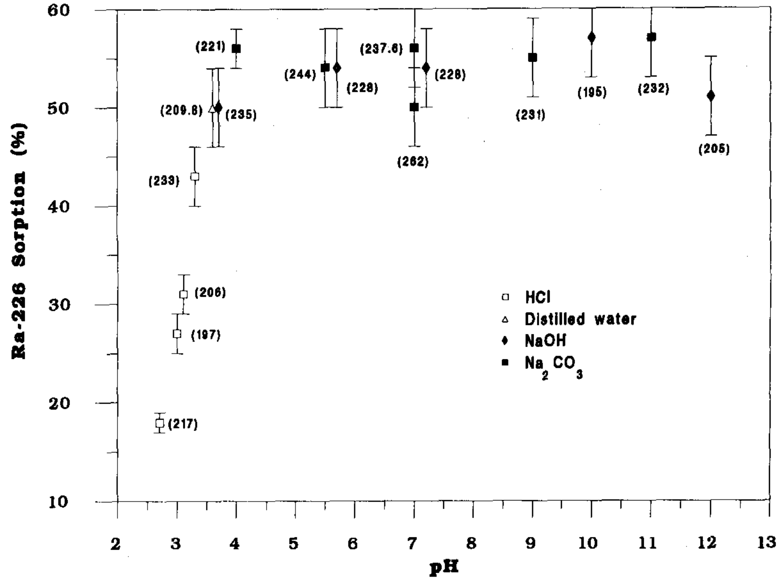

Fig. 7 ^{226}Ra sorption on MnO$_2$ as a function of pH. Height of MnO$_2$ column: 35 mm, 12.6 mm i.d. Numbers in parenthesis represent flow rate (mL min^{-1})

Table 1
Chemical concentration of the simulated groundwater

Cations	Concentration (mg L^{-1})	Anions	Concentration (mg L^{-1})
Na$^+$	580	Cl$^-$	685
K$^+$	16	HCO$_3^-$	1015
Ca^{2+}, Mg^{2+}	80	SO$_4^{2-}$	60

charge on the surface will remain negative at a pH of 2 thus facilitating cation adsorption. But some authors suggested ^{226}Ra sorption increases with increasing pH of the solution[5,7].

Sorption behaviour of ^{226}Ra on MnO$_2$ as a function of the types of water. Environmental waters contain a significant amount of dissolved cations and anions of varying concentrations. These cations may compete with Ra^{2+} ions for sites/vacancies thus limiting the sorption potential for ^{226}Ra. An experiment was carried out to examine any variations in the sorption of ^{226}Ra on MnO$_2$ in different types of waters. Three types of waters were used to cover the wide spectrum of environmental waters. These include distilled water, tap water and simulated groundwater having specific conductivities of 2, 330 and 3000 μS cm^{-1} respectively. Simulated groundwater was prepared to resemble spa water which is known to contain elevated levels of ^{226}Ra. The types and typical concentrations of ions used in the preparation of the simulated groundwater are shown in Table 1. The three waters were spiked with ^{226}Ra and were passed through the MnO$_2$ at a constant flow rate. Tap water was used since it contains a variety of transition metals (eg. manganese and iron) and barium at trace levels which are known to be competitors/scavengers that affect the radium sorption on manganese dioxide. The conditions and the results of the experiments performed is shown in Table 2.

The results show no variation in sorption of ^{226}Ra in MnO_2 using the three types of water, suggesting that there is no competition between Ra^{2+} ions with other ions for site/vacancies in the MnO_2. The results also indicate that pH has no influence on the sorption process. This supports the measurements in the pH section, showing the sorption remains constant when the pH is maintained above 3.6. It can be concluded that the chemical nature of the waters tested, i.e. its pH and the type and amount of chemical species present had no influence on the sorption uptake of ^{226}Ra by MnO_2 at the activtites used in this experiment. Since the pH range of most environmental waters lie in the neutral and slightly acidic regions (pH 6 - 8) and most types of environmental waters have conductivities below 5000 µS cm^{-1}, this provides encouraging practical applications in preconcentrating ^{226}Ra from environmental waters on MnO_2.

Table 2

^{226}Ra sorption measurements on MnO_2 using different waters

Mass of solution: 750.0 g. Height of MnO_2 in column: 65 mm. Internal diameter of column: 9.25 mm

Type	pH	Flow rate (mL min^{-1})	^{226}Ra activity in feed solution (Bq)	^{226}Ra sorption (%)
Distilled water	10.0	180.2 ± 0.4	255	62 ± 3
Tap water[a]	7.2	189.0 ± 0.6	260	64 ± 4
Simulated groundwater[a]	7.6	190 ± 1	250	62 ± 3
Simulated groundwater	10.0	162.2 ± 0.2	260	63 ± 4

[a] No bicarbonate/carbonate buffer added to the system

Sorption behaviour of ^{226}Ra on MnO_2 as a function of flow rate and contact time: To the best of the author's knowledge, no studies which examined the relationship between sorption measurements of ^{226}Ra as a function of contact time on manganese dioxide by the use of columns have been performed. Since column experiments can be advantageous in preconcentrating ^{226}Ra from large volumes of water in a wide range of applications, it is essential to understand the relation between the sorption uptake and contact time. This study will provide a basis for understanding the relationship of the sorption of ^{226}Ra on MnO_2 as a function of flow rate and contact time. The sorption experiments involved the use of four different size columns. The first column has 65 mm height and 9.25 mm i.d.; second column has 35 mm height and 12.6 mm i.d.; third column has 24 mm height and 15.9 mm i.d.; fourth column has 16 mm height and 19.0 mm i.d., whereby a constant mass of 10.00 g was placed in the columns. Tests were performed by spiking ^{226}Ra in a constant mass of 750.0 g of simulated groundwater (see Table 1). The conditions of the experiment were remained constant as described. The results of this experiment are shown in Fig. 8.

The results in Fig. 8, show that increasing the flow rate of solution through the MnO_2 column results in a decrease in the percentage of ^{226}Ra sorption. This is explained by a decrease in contact time of solution with MnO_2 thus limiting sufficient time for the sorption of Ra^{2+} ions. Greatest sorption of ^{226}Ra on MnO_2 was obtained in column 1 (height = 65mm, internal diameter = 9.25mm) of 92% to 38% at flow rates of 16.22 mL min^{-1} to 966 mL min^{-1}, respectively. The flow rate (Q) of solution passing through the MnO_2 column of known height (h), diameter (d) and area (A) for a constant volume (mass = 10.00 g) of MnO_2 occurs

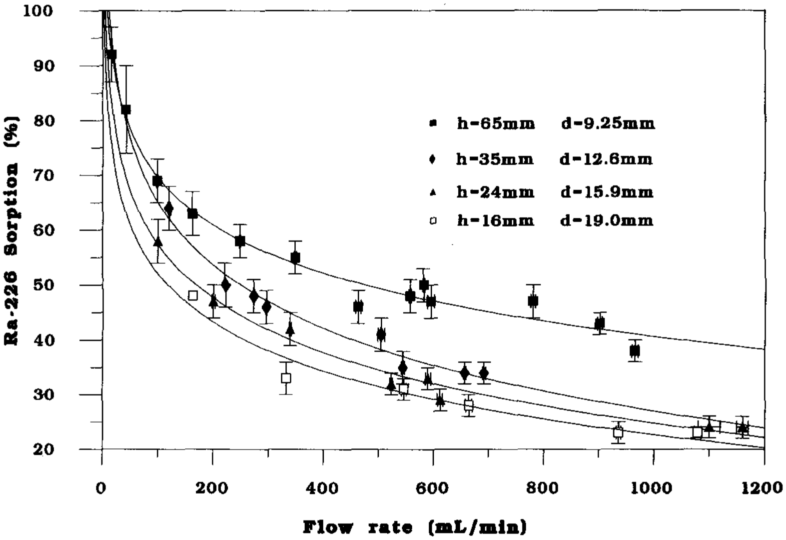

Fig 8. ^{226}Ra sorption on MnO_2 as a function of flow rate for various size columns

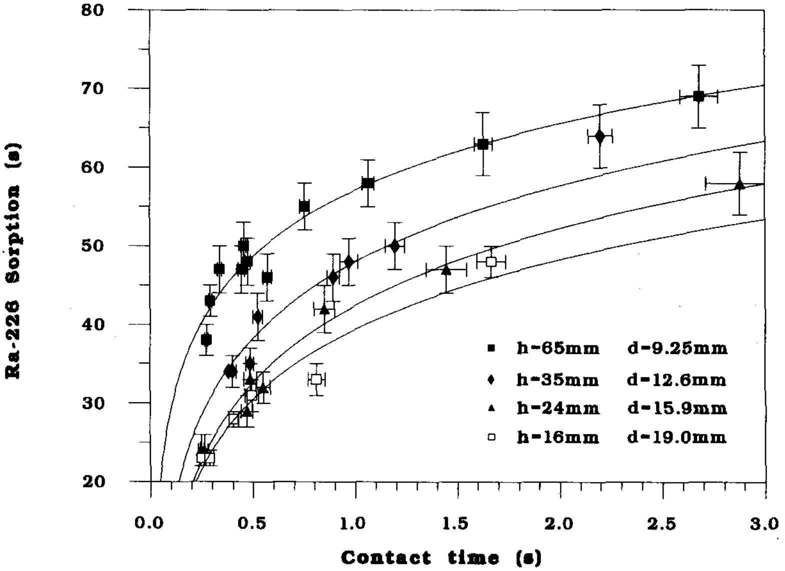

Fig. 9 ^{226}Ra sorption on MnO_2 as a function of contact time for various size columns at known velocity (v) and contact time (T) as shown by the following equations:

$$Q = vA \tag{1}$$

$$T = \frac{Ah}{Q} = \frac{h}{v} \tag{2}$$

Using Eq. 2, the contact times of water solution with MnO_2 can be determined for the various size columns. From these calculations a plot of sorption of ^{226}Ra on MnO_2 as a function of contact time was constructed as shown in Fig. 9.

Figure 9 reveals the sorption of ^{226}Ra in MnO_2 increases with longer contact times. In column 1, sorptions of 92-38% were obtained at contact times of 16.2 - 0.273 s respectively. In Figs. 8 and 9, a fixed volume of MnO_2 was used. Thus at constant flow rate the contact times of water within the MnO_2 for all columns will be the same (see Eqs. 1 & 2). Since both plots show the column with the greatest height (ie. h=65mm, d=9.25mm) had the largest sorption, the height may have an influence on the sorption amount. From these observations a plot of ^{226}Ra sorption as a function of height/diameter (h/d) ratio was plotted for known flow rates (see Fig. 10). In Fig. 10, it shows at higher flow rates (Q=500 mL min^{-1} & 1000 mL min^{-1}), the height factor has greater influence on sorption as shown by an increase in sorption. While at a slower flow rate (Q=100), the height factor has less relevance on the sorption amount (ie. reaches a plateau). This suggests that at slower flow rates all columns behave similarly (see Fig. 8) while at higher flow rates the longest column will have the greatest sorption (see Figs. 8 & 9). Hence it can be concluded that sorption depends strongly on the time that the solution is in contact with the MnO_2.

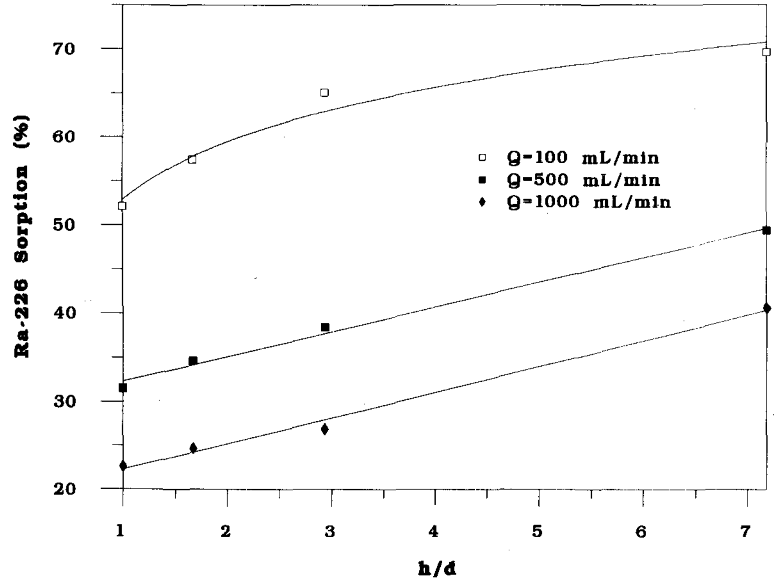

Fig. 10 ^{226}Ra sorption on MnO_2 as a function of h/d ratio for various flow rates

Conclusion

A study of ^{226}Ra sorption on MnO_2 was undertaken using both batch and column tests under a variety of conditions. The results indicate that chemical and/or specific sorption process(es) are the dominant mechanism(s) and the sorption amount showed no dependence on ^{226}Ra activity, chemical species, types of water and pH when this exceeds 3.6. The sorption was greatest in columns as compared to the batch tests at comparable contact times which may be as a result of more thorough mixing of ^{226}Ra with the MnO_2 material within the column. The column tests indicate the sorption is largest in the column with greatest height of MnO_2. Since no known study has shown sorption studies using columns under a variety of conditions, it is difficult to provide comparisons and reasons for variations in sorption in columns of different geometries for the same contact time. The height of the MnO_2 shows an important influence on the sorption amount of ^{226}Ra on MnO_2. A possible explanation is that the sorption in the MnO_2 material obeys an exponential law (eg. Beer's law), whereby greater sorption occurs at the top portion of MnO_2 and the sorption decreases exponentially as the solution passes through the MnO_2 column. This provides a possible explanantion for the dependence of sorption on the height. Tests need to be undertaken whereby ^{226}Ra spiked solution is passed through a segmented column of MnO_2 at various flow rates so as to obtain sorption profiles. This exercise is beyond the scope of the paper but it will be undertaken in a future study.

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