Application of weak-acid cation softener in radium removal from ground water

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Abstract

A pilot scale ion exchange unit, based on a single-bed weak-acid cation exchange resin, was designed and tested in the field to remove combined radium from raw ground water where radium content exceeds the national regulation limits set for radium in drinking water. The resin could efficiently perform 10 resin exhaustion–regeneration cycles, with an effluent/waste ratio of about 138 in each cycle, before 5 pCi/L radium breakthrough. Simultaneous reduction in the total hardness and total dissolved salts was also observed. The waste brine could be environmentally reclaimed. Based upon the obtained results, some conclusions and recommendations are drawn.

Keywords: weak-acid cation-exchanger, softener, radium removal, water treatment.

1   Introduction

Radium is an alkaline earth metal of high radiotoxicity and commonly found in ground water as divalent cation. The chemical behaviour of radium is similar to that of calcium and magnesium, the principal components of hardness. Thus, processes that are used to soften hard water are useful for removing radium from drinking water. According to the national and American regulations [1, 2], naturally occurring radium exceeds the maximum contaminant level (MCL) of 3 pCi/L for ^{226}Ra and 5 pCi/L for combined radium (^{226}Ra + ^{228}Ra) is reported in some counties of the central province of Saudi Arabia [3]. Activity concentration up to 3.1 and 4.8 Bq/L of ^{226}Ra and ^{228}Ra, respectively, were found, depending upon the well depth. Several habitation sites are randomly dispersed in these counties, including big cities, small towns, villages and minor communities.

However, an appropriate and generally applicable technique for treatment of this raw water is required to remove radium, aiming at producing water of drinking quality. Several methods have been identified as treatment techniques, such as distillation, filtration, precipitation, ion exchange, adsorption, etc. The technique of choice usually depends upon the characteristics of water and the contained radionuclides.

The treatment technique used in the water treatment station in the central province of Saudi Arabia is the traditional technique that depends upon aeration of the raw water in the concrete tower to oxidize the iron and manganese to hydrated oxides. These oxides are precipitated and any suspended particulates are removed by filtration via sand filters before pumping of the product water into the municipal distribution network. The particulates of the precipitated or suspended hydrated oxides are efficient absorbents to radium, which is partly removed simultaneously with the particulate matter. The particulates that are continuously accumulated, together with radium, on the filter-sands resulted in radon release into the product water in concentrations that may exceed that of the feed water, especially in the pre-exhaustion stages of these filters. Due to this continuous accumulation, the exhausted filter sands are periodically replaced, which has resulted in a huge amount of contaminated sands (now about 3500 m^3) around the work site. The sand exposes workers to radiation and radon inhalation. The disadvantages of the sand filter technique gave rise to the need to improve these water works by testing other techniques to be used as an alternative. Thus, due to the widespread dispersion of various small communities over a vast arid area, special respect should also be given to small portable, economically reasonably point-of-entry water treatment processes.

In this context, it is reported [4, 5] that for bicarbonate containing water, weak acid cation exchange (WAC) resins, in the H$^+$ or Na$^+$-form, have a very high ion exchange capacity and are very selective to divalent and trivalent cations and hence can efficiently remove radium, barium and hardness (Ca and Mg) in addition to iron from water and produce a minor radioactive waste-body. It can also remove alkalinity, reduce total dissolved salts and is easily regenerated. These advantages justify testing the application of this technology. However, the objective of this work was to investigate and document the performance of WAC resin for removing radium and to monitor the simultaneous impact of this treatment process on the total dissolved salts and the total hardness of this water under field pilot-scale controlled operating conditions. Pilot-scale operations help one to understand and solve problems similar to those likely to be encountered during full-scale operations.

2 Experimental

A weak-acid cation exchange resin, Purolite C-104 from Dow Company, in the H$^+$-form, was used in all experiments as a single bed. The resin is made from a macroporous acrylic polymer, crosslinked with divinyl benzene (DVB) and functionalized with carboxylic exchange groups. It can be economically regenerated by an upflow countercurrent technique. Weak acid cation exchange

resins have the highest capacity of any ion exchange material yet invented [4]. According to the manufacturer specifications, the minimum capacity is 9.8 eq/dry kg. The shipping weight (in the H^+-form) is about 745 g/L for the used size (16-50 mesh).

According to the manufacturer of the ion exchange resin, a pilot-scale single bed ion exchange unit was designed (Fig. 1) where the minimum bed depth should be not less than 700 mm, however, a column of 40 mm in diameter and 1 m in height was used. One litre of resin bed volume (BV) gave a bed of 800 mm in depth and was used for the whole work. The feed water (influent) passes through a preliminary microfiltration membrane filter before loading to the ion exchange column, to guarantee complete suspension and oil removal. The product water (the effluent) passes through autosampler to collect, automatically, 1L samples for routine analysis in order to follow up the system performance.
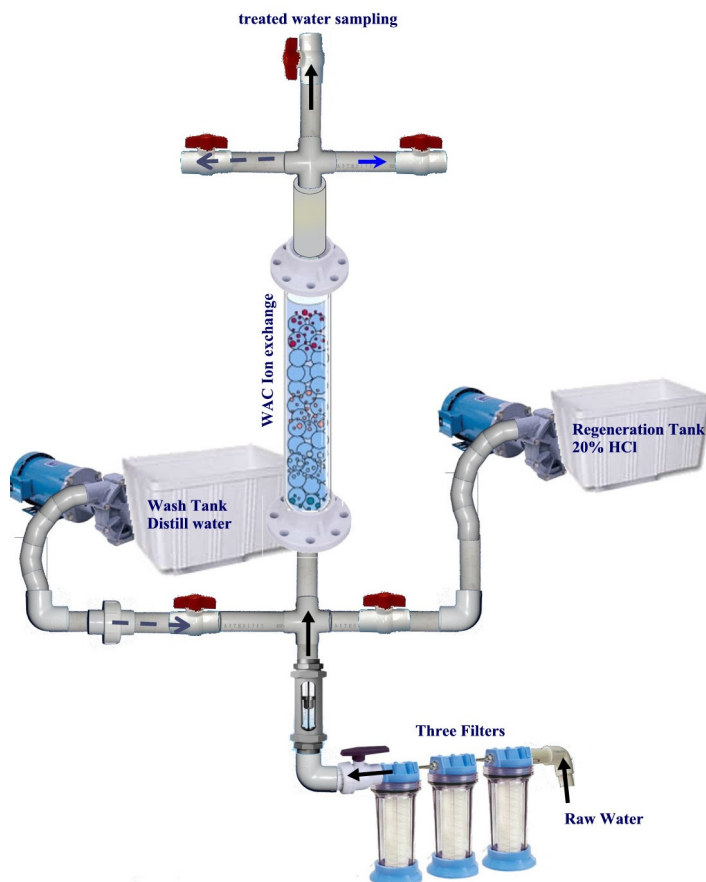

Figure 1:   Diagram of the pilot-scale ion exchange unit.

Radium-228 and ^{226}Ra were determined in feed water by γ-spectrometry. Due to the very low guideline values [1] set for ^{226}Ra and ^{228}Ra in drinking water, a more sensitive technique was required to meet these regulation-limits in the product water. Radium-226 was determined in the effluent by α-spectrometry as a very sensitive technique. The analytical procedure is described elsewhere [6, 7].

Based on the fact that chemically, the isotopes of radium are indistinguishable by the exchanger, thus, removing some percentage from ^{226}Ra means removing the same percentage from ^{228}Ra. It is a helpful fact when monitoring treatment processes for total radium removal because ^{226}Ra analysis is easier, more sensitive and less expensive than ^{228}Ra analysis. However, in this work the concentration of the combined radium in the product water was calculated from the measured ^{226}Ra concentration in the product water and the ^{228}Ra/^{226}Ra isotopic ratio in the feed water, which should be similar to that in the product water.

Sulphates were determined by a modified turbidimetric technique [8, 9]. Bicarbonates were measured by acid titration at pH 4.8. Mn and Fe were measured by atomic absorption spectrophotometry. Chlorides were determined by silver nitrate titrations using potassium chromate as an indicator.

A Canberra model S470 "Alpha Analyst" high-resolution α-spectrometry system was used to measure the α-emitter ^{226}Ra. The system consists of eight 450 mm^2 silicon surface barrier detectors. Each pair of detectors is located in the same chamber with a partition. The system is fully computer-controlled and automatically manages the spectra, using an OS/2 operating system, a Genie-PC and Alpha Analyst software. The minimum detectable activity (MDA) for the eight detectors ranged from 6-10 mBq//L (0.16-0.27 pCl/L), for 18 hours counting time and 150 mL sample size. The efficiencies of the detectors in the chosen configuration ranged from 20.4 to 21.1% with a quite satisfactory resolution of about 35-50 keV for the 5.305 MeV alpha particles of ^{210}Po. A motor-driven vacuum pump provided adequate evacuation (10^{-2} mm Hg) of the vacuum chambers of the system was used.

A high-resolution hyper pure germanium γ-spectrometer, CANBERRA type, Model No. GX 4014 with a beryllium window, connected to a personal computer, was used to measure ^{226}Ra and ^{228}Ra in the feed water. The energy resolution of the spectrometer was better than 1.9 keV for the 1332 keV γ-ray photo peak of ^{60}Co and the relative efficiency was about 40%. The minimum detectable activity of the system for measuring ^{228}Ra was about 0.5 Bq/L for 6 h count time and 500 mL sample size.

Atomic absorption spectrophotometer, Model AAS 400 with an autosampler Model AS 93 plus (from PerkinElimer) and a graphite furnace, Model HGA 900, with an autosampler, Model AS 800, were used for analyzing the inactive metals.

3 Results and discussion

Due to the fact that the efficiency of removing chemical species from water by ion exchange depends upon its concentration in the feed water, variation in the

characteristics of the feed water, especially the water burden of the cations of higher selectivity, will affect the breakthrough capacity of their removal. However, the feed water from deep wells (1000-1400 m in depth) was subjected to repetitive investigation (six investigations from April 2005 to March 2006) to document the variation in water characteristics during the different seasons and the results are given in Table 1. The data show that the water content of the different ions varied within a considerable range. No relation was observed between the variation in water characteristics and seasons. Considering the species of interest, the maximum recorded concentration of total dissolved salts (TDS), total hardness (TH), Ca, Mg, Ba and Ra in the repetitive measurements exceeded their minimum recorded concentration by about 15.5, 14.0, 18.8, 26.3, 18.2 and 31.8%, respectively.

Table 1:   The analytical data of the feed water according to repetitive measurements within a year.

Analyte	Concentration, mg/L	
	Minimum	Maximum
TDS	619	715
TH	250	285
Ca	69	82
Mg	19	24
Ba	0.11	0.13
^{226}Ra*	36	47
^{228}Ra*	55	73
Combined Ra*	91	120
Fe	1.2	2.1
Mn	0.33	0.54
Na	97	130
HCO_3^-	222	245
SO_4^-	100	121
Cl^-	107	135

* Concentrations of radium isotopes and combined radium are in pCi/L.

For testing WAC resin in radium removal, controlled laboratory bench-scale operating research work was first attempted to determine the factors that affect the resin performance in the treatment process. Unfortunately, this was excluded due to the fact that transportation subjected the feed water to aeration and cooling resulted in iron and manganese precipitation, as hydrated oxides. This precipitation changed the feed water characteristics and has disturbed the typical conditions. However, a pilot-scale ion exchange unit was designed and directly tested in the field.

The chemical behaviour of barium and radium are very similar and are much like those of calcium and magnesium, the principal components of the hardness in water. Therefore, the breakthrough capacity (the effluent quantity not

exceeding the MCL) of radium removal in one cycle was tested. The breakthrough capacity is usually expressed in the number of treated BVs. Influent water, with typical composition given in Table 2, was used in this work.

On loading the feed water (pH 8.3±0.2), gas bubbles were formed inside the column due to the resin/bicarbonate reaction and release of carbon dioxide gas. Some of the formed gas bubbles were trapped inside the column resulting in a decrease in the solid/water interface contact area leading to a reduction in the ion exchange capacity of the resin. Pumping the wash water (tap water) upflow countercurrent has removed the gas bubbles.

The 5 pCi/L breakthrough capacity for radium removal was found to be about 1100 BV of processed water at a preliminary flow rate (expressed as the empty bed contact time, EBCT) equals 1.5 minutes. This rate corresponds to a flow rate of 0.65 L/min. The pilot plant showed a reduction in radium concentration from 98 pCi/L to < 5 pCi/L in the product water. The resin swelled up to about 15% more than its normal size at the end of the cycle, and was regenerated by 5 BV of 4M HCl solution and washed by 4 BV of tap water, where the resin shrank again to its normal size. Therefore, enough space was left inside the resin cartridge for resin expansion. The regenerant was pumped upflow countercurrent at a rate of (0.7 L/h).

Many factors control the economy of the ion exchange treatment processes, such as the breakthrough capacity of the interest species removal, the number of satisfactory resin exhaustion/regeneration cycles that can be achieved, the nature and the size of the regenerant and generated waste, manpower, the consumption of chemicals and other materials, etc. In this context, breakthrough capacity and the number of normal exhaustion/regeneration cycles are prime factors in evaluating the resin performance. Ten exhaustion-regeneration-brine reclamation cycles were tested in this work. Purolite C-104 could easily perform ten exhaustion-regeneration cycles with about 1100 BV breakthrough capacity in removing radium (Fig. 2). The performance of the resin in the 1st and 10th cycles
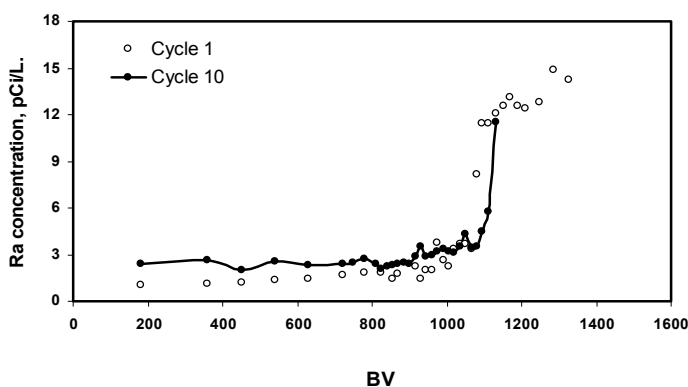

Figure 2:   Breakthrough curves of radium removal process by Purolite C-104 in the 1st and 10th cycles.

were almost the same, indicating excellent performance and reversibility in the first 10 cycles and also indicating that the resin can be used over and over again making the process most economic.

Table 2:   A typical analytical data (ppm) of the feed and product waters in the ion exchange process under their controlled conditions.

Analyte	Feed water	Product water*		MCL
		Concn.	% removal	
TDS	681	500	26.6	1500
TH	265	57	78.5	500
Ca	71.3	17	24.5	200
Mg	23.5	9	63	150
Ba	0.105	0.007	93.3	2.0
^{226}Ra**	39.5	1.5	96.2	3.0
^{228}Ra	58.4	-	-	-
Combined Ra	97.9	3.7 (<5)	96.2	5.0
Fe	1.5	0.006	99.6	0.3
Mn	0.351	0.003	98	0.05
Na	112	112	00.0	200
HCO_3^-	231	< LLD	100	500
SO_4^-	100	100	00.0	400
Cl^-	115	115	00.0	250

* The analyzed product water was the 960th BV of the 10th cycle.
** Concentration of radium isotopes and combined radium are in pCi/L.

From the characteristics of the water produced by ion exchange using WAC (Table 2), it is clear that the ion exchange technique is efficient in removing radium and alkalinity and also in reducing TDS and TH. The back release of radon from the sand filters to the product water in the conventional technique could be avoided by using this ion exchange technique.

As mentioned before, the characteristics of feed water, especially the water burden of total dissolved salts, will affect the efficiency of the treatment process. Total hardness is the most effective parameter controlling the breakthrough capacity of radium removal due to the unusually high selectivity of the resin to the divalent and trivalent cations, when operated in neutral or slightly basic media [5]. The higher the TH the lower will be the breakthrough capacity of removing radium and the other divalent cations and vice versa. In the present work, the repetitive measurements of the feed water showed that the variation in the TDS concentration ranged from 619-715 mg/L and in the TH ranged from 250-285 mg/L (Table 1). However, the variation in the breakthrough capacity for Ra removal due to the variation in the TH concentration in feed water can be

estimated based on the logic principal that "in any cycle, the amount of hardness absorbed by the resin (resin capacity, in mg) before radium start to breakthrough is almost constant and equals the difference between the TH concentration (in mg/L) in the influent (C_i) and that in the treated effluent (C_e) times the volume (V) in litres of that effluent". It can be expressed by the following equation:

$$\text{The resin capacity} = (C_i - C_e)V \tag{1}$$

The minimum volume that could be treated within one cycle will be at maximum TH concentration. Assuming that the variation in the TH concentration of the treated effluent (C_e) due to variation in the TH concentration of the feed water (C_i) is minor and can be neglected, equation (1) can be expressed as:

$$\text{The resin capacity} = (C_i - C_e)V = (C_{i\,min} - Ce)V_{max} = (C_{i\,max} - C_e)V_{min} \tag{2}$$

where $C_{i\,max}$ and $C_{i\,min}$ are the maximum and minimum TH concentrations recorded in the repetitive measurements of the influent, respectively (Table 1), and V_{min} and V_{max} are the corresponding estimated minimum and maximum volumes of the treated effluent in one cycle, respectively. From equation (2):

$$V_{max} = [(C_i - C_e)\ V]\ /\ (C_{i\,min} - Ce) \tag{3}$$
$$V_{min} = [(C_i - C_e)\ V]\ /\ (C_{i\,max} - Ce) \tag{4}$$

Accordingly, and according to the data presented in Table 2, in the 10th cycle, the breakthrough capacity was 1100 BV (or 1100 L, where 1BV equals 1L) when the TH concentration in the influent was 265 mg/L and will be varied up and down according to the TH concentration in the feed water. Using this data and the maximum and minimum values recorded in the repetitive measurements (Table 1) for TH concentration, the maximum and minimum breakthrough capacities of the radium removal under these operation conditions can be estimated (using equations (3) and (4)) as 1185 and 1003 BV, respectively. In other words, the minimum breakthrough capacity estimated for radium removal (resin exhaustion capacity) is 1003 BV, which will be guaranteed in all cases and used as a guideline limit recommended to be strictly followed by the common operators for resin regeneration. A single unit can be used as a small portable economical treatment system to produce water of drinking quality for small communities in remote areas. For a larger production capacity, a multiple system can be used by connecting several units in parallel, where the number of units and the volume of the resin bed in each unit can control the production capacity.

4 Conclusion

The application of the weak acid cation exchange resin, Purolite C-104 in the H^+-form, for radium removal from bicarbonate containing ground water showed 10 exhaustion-regeneration cycles with excellent performance and reversibility. About 1100 BV were treated in each cycle. About 1003 BV was the minimum

limit estimated for resin exhaustion. The resin can be used over and over, indicating economic application. An advantageous effluent/waste ratio of about 122 in the first cycle and about 138 in the next cycle was obtained. About 78% of the total hardness and about 27% of the total dissolved salts were simultaneously reduced with radium removal. The resulted brine waste was easily environmentally reclaimed, whereas the minor radioactive waste-body was isolated.

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