키토산 비드를 이용한 지하수중의 우라늄제거에 관한 연구

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Introduction

Overview

- The health and environmental protection agencies have recommended safe limit of uranium in drinkingwater for human beings
- The World Health Organization(WHO 1998) and the United States Environment Protection Agency (USEPA 1992) in general have recommended 2㎍/l of uranium concentration in drinking water as the safe limit
- Recently a country presented research report(The Institute for Environmental Research 1999~2002) shows the actual condition of radioactive pollution on groundwater
- Natural uranium consists of a mixture of three radioactive isotopes which are identified by the mass numbers 238U(99 2836% by mass) 235U (0 711%) and 234U(0 0054%)
- These radionuclides have very long half-lives 4 5×109 7×108 and 2 5×105 years respectively
- Uranium as a natural component of the human environment is likely to be presented in trace amounts in all foodstuffs and consequently as a result of intake of water food and air also presented in the human body It has been estimated that the total annual intake of uranium into the human body by adults is about 460㎍ by ingestion of food and water and because of low air concentration only about 0 6㎍ from inhalation (Fleenne et al , 1987 UNSCEAR 2000a b Pietrzak –Flis et al 2001)

Introduction

Target

This study suggests strongly that chitosan and grafted chitosan with itaconic acid are very useful to purification of water particularly groundwater or natural water contaminated with uranium

Background

The value of water quality standard on radioactive in drinkingwater

Nation / a head	unit	WHO	USA	Canada	Korea
Gross Alpha Particle activity	pCi/L	2 7	15	–	–
226Rn 228Rn	pCi/L	–	5	1 –	–
U	ppb	–	(20)	100	–
Rn	pCi/L	–	(3000)	–	–

* ( ) is the proposal value of water quality standard,

pCi = picocuries

Background

Uranium concentrations in groundwaters (unit ppb)

Areas	n	Mean±S D	(min ~ max)	GM***	Median	5%tile	95%tile
Seoul	75	9 78±44 76	(N D ~322 00)	0 25	0 30	N D	43 40
Gyeonggi Gangwon	80	1 29±4 07	(N D ~31 90)	0 13	0 19	N D	5 30
Pusan Gyeongnam	80	1 45±6 97	(N D ~58 10)	0 18	0 18	0 01	2 29
Daegu Gyeongbuk	109	0 69±1 24	(N D ~6 20)	0 12	0 12	N D	4 04
Gwangju- Jeonnam	66	1 17±3 69	(N D ~25 10)	0 08	0 05	N D	4 56
Jeonbuk	41	1 49±2 35	(N D ~7 82)	0 02	0.21	N D	7 18
Chungnam	54	0 87±1 83	(N D ~9 67)	0 15	0 17	N D	0 01
Daejeon	17	44 09±98 87	(0 020~402 30)	3 75	13 70	0 02	402 30
Chungbuk	77	1 38±3 60	(N D ~22 80)	0 26	0 36	N D	4 83
Jeju	12	0 04±0 06	(N D ~0 23)	0 02	0 02	N D	0 23
Total	611	3 39±23 82	(N D **~402 30	0 18	0 19	N D	7 32

*p<0 0001 Kruskal-Wallis test **Not Detected(<0 012ppb) ***Geometric mean

Data source The Institute for Environmental Research, 1999~2002

Background

Uranium concentration in drinkingwater

Company(goods name)	uranium(ppb)
Ilwha	4 83
Joowon mineral drink	22 80
Korea chungjung drink	24 10
Haksan zeolite	9 67
geukdo drink	7 29
Salsong(Dongwon drink)	25 10
Ohksoo drink	8 62

(Data source watersource environment 2002 2)

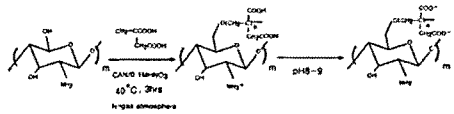
Background

Treatment methods for uranium removal from drinking water

Treatment Method	Removal(%)	Special Condition/Notes
Iron coagulation	80~85	pH 6 and 10
Alum coagulation	90~95	pH 10
	80~85	pH 6
Lime softening	99	pH 10 6 + Mg ion
Cation exchange	80~85	
H^+ form	90~95	pH 3 5
Ca^+ form	70	pH 4
Na^+ form	70~85	pH ≤ 7
Anion exchange	99	1 000~50 000 BV
Activated alumina	99	1,500~2 000 BV
GAC	90+	Limited capacity
Reverse osmosis	99	None

7

Schematics of graft-copolymerization reaction



8

Materials

▶Test water

Dissolving mixture of Plasma Emission Standard Uranium (1 001㎍/㎖, matrix 5% HNO_3 VHG LABS, Manchester product No PUN-100) in Distilled water solubled 1㎖/ℓ solution

- $UO_2(NO_3)_2$ 1ppm solution

▶Groundwater

Sampling water in Namgu Duwangdong Woolsan(contained U 38 8 ppb)

▶ All other materias used were of analytical reagent grade

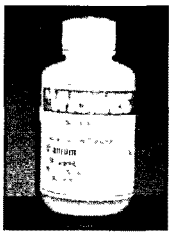


Fig Plasma Emission Standard Uranium

9

Experiments

Preparation of chitosan Beads

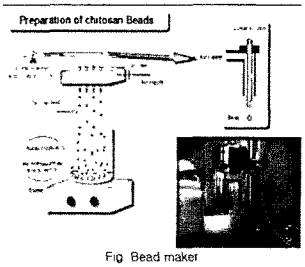


Fig Bead maker

10

Experiments

Graft-copolymerization

The conditions of graft copolymerization are

amount of chitosan 2g/batch

amount of each monomer 1 7422g batch

concentration of ceric ammonium nitrate(CAN) 3 33x10⁻³moles batch

- Dissolving mixture of chitosan and monomer in dilute acetic acid solution
- ↓
- Swelling
- ↓
- Adding reaction initiator
- ↓
- Reaction for more than 3hrs
- ↓
- Precipitation in acetone
- ↓
- Filtration
- ↓
- Washing off homopolymer or other contaminants
- ↓
- Vacuum drying

Fig Flow sheet of graft-copolymerization of itaconic acid onto chitosan

11

Experiments

- Dissolving mixture of chitosan 2 5%(w/v) and Aetic Acid 4%(v/v) /Dissolving itaconic acid grafted chitosan 2 5%(w/v) in water
- ↓
- Filtering
- ↓
- Dropping in NaOH/EtOH/H_2O(4/20/76% w/v/v) solution
- ↓
- Reaction(12hr neglect)
- ↓
- Washing (pH 7 distilled water)
- ↓
- Washing (EtOH)
- ↓
- Washing (dimethylformamide, DMF)
- ↓
- Swelling(24 hr) in DMF
- ↓
- Addition Hexamethylene diisocyanate
- ↓
- Reaction(24hr)
- ↓
- Washing (EtOH)
- ↓
- Washing (Distilled water)

Fig Preparation method of chitosan beads and itaconic acid grafted chitosan beads

12

Methods

The methods applied in this experiment are

1 Preparation of chitosan and chitosan grafted with itaconic acid by Graft-copolymerization
2 Preparation method of chitosan beads(Cs) and chitosan grafted with itaconic acid beads(Csia)
3 Adsorption equilibrium
  - Effect of crosslinking degree on the adsorption of uranium
  - pH effect on the uranium adsorption
4 Adsorption velocity
  - Uranium uptake with various of crosslinking degree
  - Uranium uptake with various bead sizes
5 Comparison of uranium removal rates with Cs and Csia, and activated carbon in a static system
6 Ability of treatment on uranium in the flow system
  - Uptake efficiencies with various of sizes of bead on test water
  - Effect of flow rates on uranium removal rates on test water
  - Comparison of uranium removal rates with Cs and Csia, and activated carbon on groundwater

13

Instrument and Analysis

- The IR spectra of Cs, Csia were obtained with a FT-IR(Perkin Elmer-1330) spectrophotometry by using KBr pellet for analysis
- Concentration of uranium was determined by Inductively coupled plasma mass spectrometry(ICP-MS , Elan-6000)
- The surface and the cross section of a chitosan bead were determined by Scanning Electron Micrography(Hitachix-650)

14

Results

Confirmation of grafted chitosan

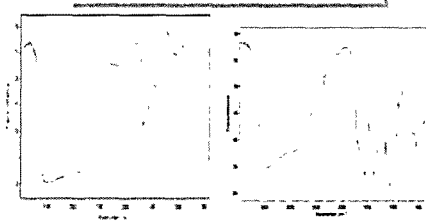


Fig FT-IR spectra of Chitosan

Fig FT-IR spectra of Itaconic acid grafted chitosan

15

Results

Adsorption equilibrium

- Cs beads(dry wet 0.5g)
- static system
- adsorption time(48hr)
- uranium concentration(1ppm)
- adsorption temp (25℃)

Degree of crosslinking(mol)	Removal rates(%)
0.05mol	97.52
0.1mol	98.48
0.5mol	98.55
1mol	98.15

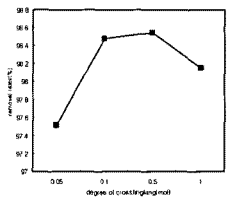


Fig Effect of crosslinking degree on the removal rates of uranium

16

Results

- Cs beads(dry wet 0.5g)
- static system
- adsorption time(24hr)
- uranium concentration(1ppm)
- adsorption temp (25℃)

pH	removal rates(%)
2	26.4
4	99.85
6	99.52
8	99.36
10	62.291
12	33.87

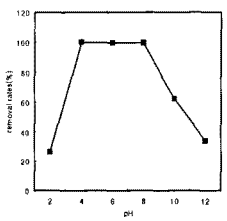


Fig pH effects on the uranium removal

17

Results

adsorption time(hr)	removal rates(%) Csia 1mm	Csia 2mm	Csia 3mm	Csia 4mm
3	71.18	71.43	75.79	76.24
6	92.79	92.14	92.3	90.08
24	99.65	98.73	98.4	98.27
32	99.98	99.61	99.11	99.11
48	99.99	99.63	99.43	99.57

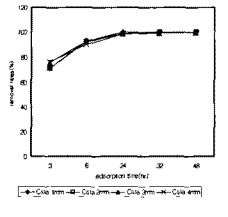


Fig Uranium removal rates with Csia bead sizes and adsorption times

18

Results

adsorption time(hr)	removal rates(%)			
	Cs 1㎜	Cs 2㎜	Cs 3㎜	Cs 4㎜
3	74 72	64 3	68 64	68 36
6	89 94	78 97	79 76	74 12
24	96 67	94 76	93 21	89 94
32	98 55	96 2	95 73	91 61
48	98 62	97 52	95 18	93 21

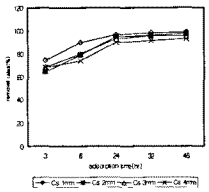


Fig Uranium removal rates with Cs bead sizes and adsorption times

Results

•Cs beads Csla beads activated carbon(dry wet 0 5g)
•static system
•1ppm of U contained 100㎖(pH 6)
•adsorption time(96hr)

Adsorption time(hr)	Removal rates(%)		
	Cs	Csla	AC
3	64 3	71 43	50 3
6	78 97	92 14	68 3
24	94 76	98 73	79 4
32	96 2	99 61	80 1
48	97 52	99 63	85 7

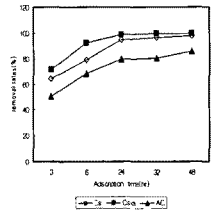


Fig Comparison of uranium removal rates with Cs and Csla and activated carbon in a static system

Results

Removal ability of uranium in the flow system

•beads packed in columns(dry wet 8g)
•filtering and controlling flow rate of test water (test water contained uranium 1ppm pH 6) passing through the filtering columns flow direct
•The experimental results explained that the efficiency of removal rate increaseed with decrease of bead size

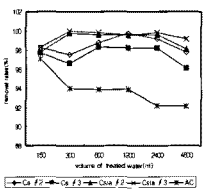


Fig Comparison of uranium removal rates with Cs and Csla and activated carbon packed in Φ4㎝× L 30㎝ column

Results

volume of treated water(ml)	U removal rates(%)			
	Cs 5ml/min	Csla 5ml/min	Cs 10ml/min	Csla 10ml/min
150	98 27	97 8	97 2	96 9
300	97 55	99 75	98 7	98
600	98 79	99 58	98 3	98 6
1200	99 75	99 56	98	98 5
2400	99 18	99 58	98 6	98 2
4800	97 81	98 1	97 5	98

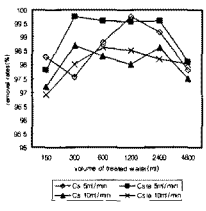


Fig Effect of flow rates on U removal rates by the beads of Cs and Csla packed in Φ4㎝× L 30㎝ columns with 1ppm U(beads size - 2㎜)

Results

•Flow rate is <5㎖/min>
•Fraction amount is <10㎖>
•The Initial conc Of U in Groundwater is <38 6ppb(pH 6)>

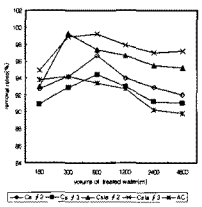


Fig Comparison of uranium removal rates with Cs and Csla, and activated carbon packed in(dry wet 8g) Φ4㎝× L 30㎝ columns

Conclusions

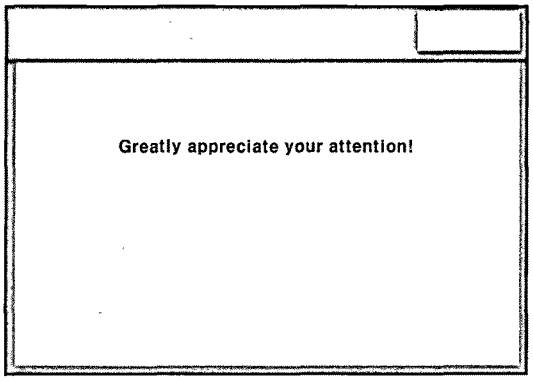
1 Characteristic absorption on the IR spectra, wave number 1650㎝-1 were assigned to the carboxyl group The IR spectra showed absorption bands at 1589 and 1650 ~1740㎝-1, attributed to the -NH2 and C=O stretching
Therefore monomers were graft-copolymerized on chitosan

2 It excepted below pH2 and the territory above pH12 and the adsorption ability was good The Optimum initial pH was 4~8

3 Uranium removal rate on bead size, the smaller the better

4 Uranium removal rate on flow rate, the slower the better

5. The chitosan grafted with itaconic acid was superior to pure chitosan in compared with uranium removal rate in the static and the flow systems Because the chitosan grafted with itaconic acid have dicarboxylic groups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