Uranium Removal from Drinking Water by Adsorption on Natural Zeolite

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Outline

- Uranium in Groundwater
- Health Effects from Uranium Exposure
- EPA Safe Drinking Water Act
- Uranium Removal from Drinking Water
  - ❑ Adsorption
  - ❑ Membrane distillation

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Uranium

- Atomic number: 92, molecular weight: 238 g/mol
- Weakly radioactive, many isotopes (U-238, >99%)
- Mainly used in nuclear fission to produce nuclear energy and (weapons) (NMSU ChE has nuclear engineering minor)
- 2-4 PPM in the Earth crust, ~40 times as abundant as silver
- Aqueous chemistry: U^{3+} (red), U^{4+} (green), UO_2^{+} (unstable), and UO_2^{2+} (yellow), only oxidation state 4 and 6 are stable.

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Uranium in Groundwater

- U leaches into groundwater from natural mineral deposits

  City of Las Cruces: 123 μg/L, EPA MCL: 30 μg/L

- New Mexico has rich uranium deposits

- Uranium production activities in New Mexico

- New Mexico depends on groundwater (Las Cruces has ~30 public wells, 300-1000 ft, from Mesilla Bolson)

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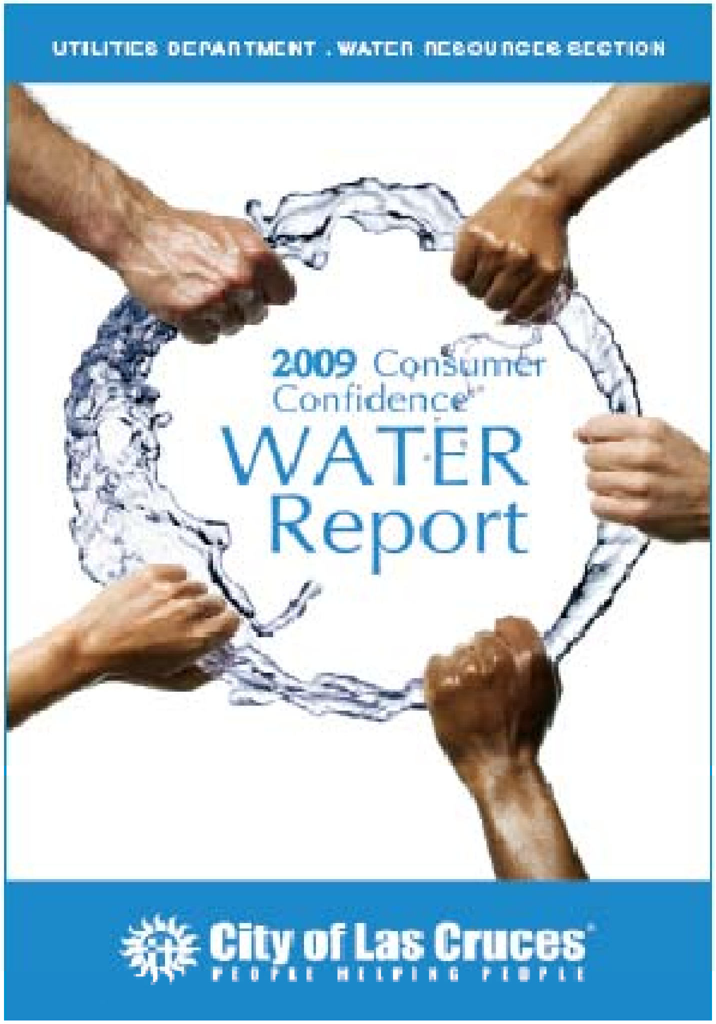
Uranium in Las Cruces Wells



Radioactive Contaminants

Contaminant	Units	MCL	MCLG	Highest Detected Levels [1]	Major Sources	Violations
Alpha emitters	pCi/L	15	0	23.5 *	Erosion of natural deposits	Yes
Radium 228	pCi/L	5	0	2.32	Erosion of natural deposits	None
Uranium	ppb	30	0	123 *	Erosion of natural deposits	Yes

* All city wells that exceeded the radioactive contaminant MCL have been taken out of service effective 12/31/06.

Alpha emitter: 23.5 pCi/L, violations: Yes

Radium 228: 2.37 pCi/L, violations: No

Uranium: 123 ppb, violations: Yes

http://www.las-cruces.org/utilities/water-report.shtm

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Uranium in Las Cruces Wells

The New Mexico Environment Department (NMED), following its initial monitoring under the new Radionuclide Rule, notified the City that **six (6) City wells exceed the standard for uranium**. This was not an immediate risk to public health. If it had been, the City would have notified the public immediately, and provided information about using an alternative water supply. However the City's water system was required to comply with the new regulation. The uranium-impacted wells have been taken out of service and the City's water system is in full compliance with the Safe Drinking Water Act, Radionuclide Rule.

http://www.las-cruces.org/utilities/water-report.shtm

U Removal Test in Las Cruces

Pilot Study Report

for

Z-92™ Uranium Treatment Process

conducted at

City of Las Cruces, New Mexico
Well No. 20

February 7, 2007

WATER REMEDIATION TECHNOLOGY, LLC

http://www.wrtnet.com/pdf/Las%20Cruces_Well%2020.pdf

http://www.donaanacounty.org/superfund/docs/UraniumTreatmentPhase2.pdf

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Uranium in Human Body

According to WHO, on average, approximately 90 μg of uranium exist in the human body from normal intakes of water, food and air; approximately 66% is found in the skeleton, 16% in the liver, 8% in the kidneys and 10% in other tissues. Daily intake of 0.5 (5) μg/kg-body does not significantly impact the kidney. (A 70 kg adult can't drink more than 1.0 L/day of Las Cruces well water)

Uranium Exposure and Retention

- **Inhalation (air)**
- **Ingestion (drinking water or food)**
- **Dermal (direct contact)**
- **Body retention**

  Most (>95%) uranium entering the body is not absorbed, but is eliminated via the faeces. Of the uranium that is absorbed into the blood, approximately 67% will be filtered by the kidney and excreted in the urine in 24 hours.

  Typically between 0.2 and 2% of the uranium in food and water is absorbed by the gastrointestinal tract. Soluble uranium compounds are more readily absorbed than those that are insoluble.

Uranium Toxicity

Chemical Toxicity (Nephrotoxicity)

50-150 mg, fatal

25-40 mg, damaged cells detected in urine

Kidney damage seems to repairable/reversible ?!

Radiological Toxicity

Alpha particles (travels less than 30 µm in the bone)

Increased risk of developing cancer during lifetime

Compound Solubility and Route of Exposure

Soluble uranium enters bloodstream/chemical toxicity

Insoluble uranium deposited in the lungs/radiological toxicity

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Health Effects of Uranium

Body system	Human studies	Animal studies
Renal	Elevated levels of protein excretion, urinary catalase and diuresis	Damage to Proximal convoluted tubules, necrotic cells cast from tubular epithelium, glomerular changes
Brain/CNS	Decreased performance on neurocognitive tests	Acute cholinergic toxicity; Dose-dependent accumulation in cortex, midbrain, and vermis; Electrophysiological changes in hippocampus
DNA	Increased reports of cancers	Increased urine mutagenicity and induction of tumors
Bone/muscle	No studies	Inhibition of periodontal bone formation; and alveolar wound healing
Reproductive	Uranium miners have more first born female children	Moderate to severe focal tubular atrophy; vacuolization of Leydig cells
Lungs/respiratory	No adverse health effects reported	Severe nasal congestion and hemorrage, lung lesions and fibrosis, edema and swelling, lung cancer
Gastrointestinal	Vomiting, diarrhea, albuminuria	n/a
Liver	No effects seen at exposure dose	Fatty livers, focal necrosis
Skin	No exposure assessment data available	Swollen vacuolated epidermal cells, damage to hair follicles and sebaceous glands
Tissues surrounding embedded DU fragments	Elevated uranium urine concentrations	Elevated uranium urine concentrations, perturbations in biochemical and neuropsychological testing
Immune system	Chronic fatigue, rash, ear and eye infections, hair and weight loss, cough. May be due to combined chemical exposure rather than DU alone	No studies
Eyes	No studies	Conjunctivitis, irritation inflammation, edema, ulceration of conjunctival sacs
Blood	No studies	Decrease in RBC count and hemoglobin concentration
Cardiovascular	Myocarditis resulting from the uranium ingestion, which ended 6 months after ingestion	No effects

Assessment of Intake and Treatment

Measurement of uranium in the urine (>0.08 μg/L)

Faecal monitoring

External radiation monitoring

Treatment

No suitable treatment for highly exposed individuals

EPA Safe Drinking Water Act

- According to the EPA Safe Drinking Water Act, anything in water that is not H_2O is considered a contaminant without regard to whether it is harmful or not.

- US EPA MCL (maximum contaminant level): **30 µg/L**

http://www.epa.gov/safewater/consumer/pdf/mcl.pdf

- World Health Organization MCL: 15 µg/L

http://www.epa.gov/safewater/contaminants/index.html

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Drinking Water Purification

Chemical methods

Chemical clarification

Physical Methods

Adsorption

Membrane filtration

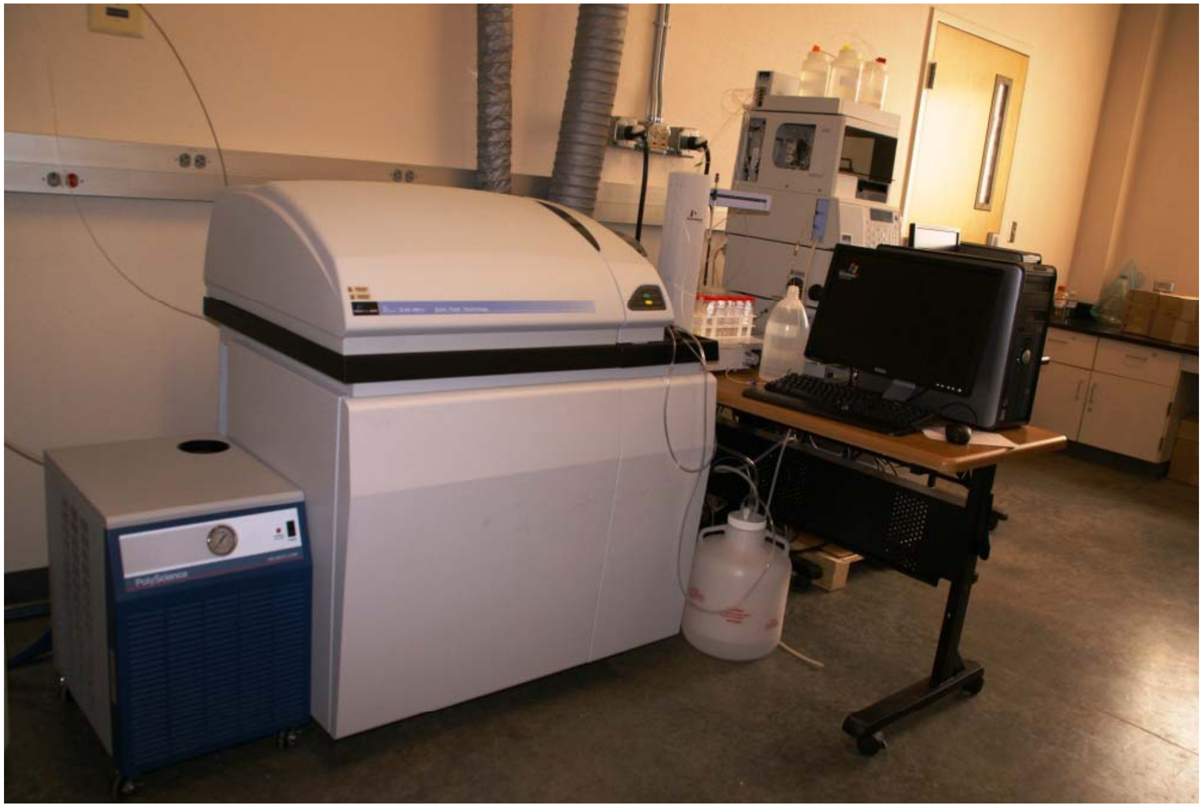
Anion-exchange

Distillation

Reverse Osmosis

Membrane distillation

Analysis of Uranium in Water



1. ASTM C1416-04(2009)

   XRF: LDL of 0.05 mg/L

2. ICP-MS

   LDL: 0.002 mg/L

3. NMSU College of Eng.

   ICP-MS – HPLC

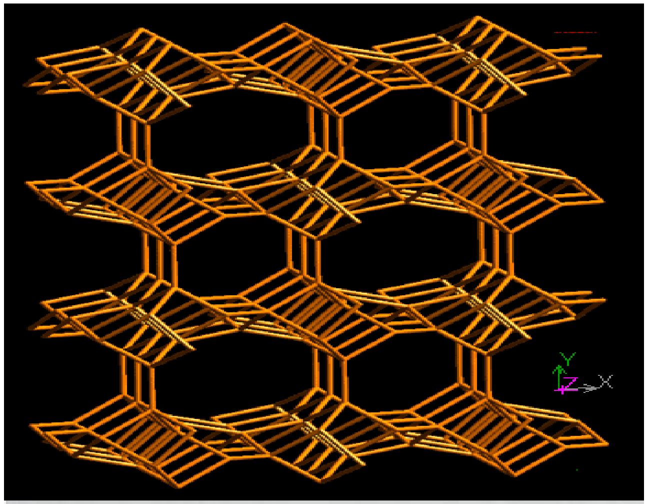
   State NM ($50/sample)

   NMSU (<$25/sample)

<u>I</u>nductively <u>c</u>oupled <u>p</u>lasma <u>m</u>ass <u>s</u>pectrometer at NMSU COE

Natural Clinoptilolite Zeolite

- $(Na, K, Ca)_{2-3}Al_3(Al, Si)_2Si_{13}O_{36}$-$12H_2O$
- Crystalline hydrated sodium potassium calcium aluminum silicate (HEU)
- Open, cage-like structures
- High cation exchange capacities
- High internal surface areas
- Available in New Mexico and Mexico

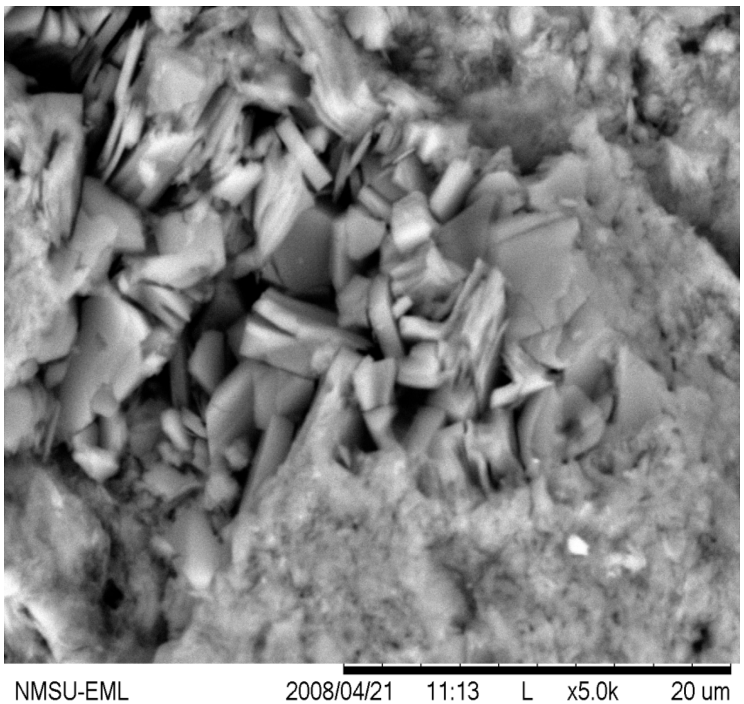


Uranium Adsorption on Natural Clinoptilolite Zeolite

- Characterize the zeolite material (XRD, XRF, SEM/EDS, N_2-Adsorption)
- Conduct batch adsorption experiments
- Analyze uranium concentration with ICP-MS
- Analyze adsorption data with isotherm models

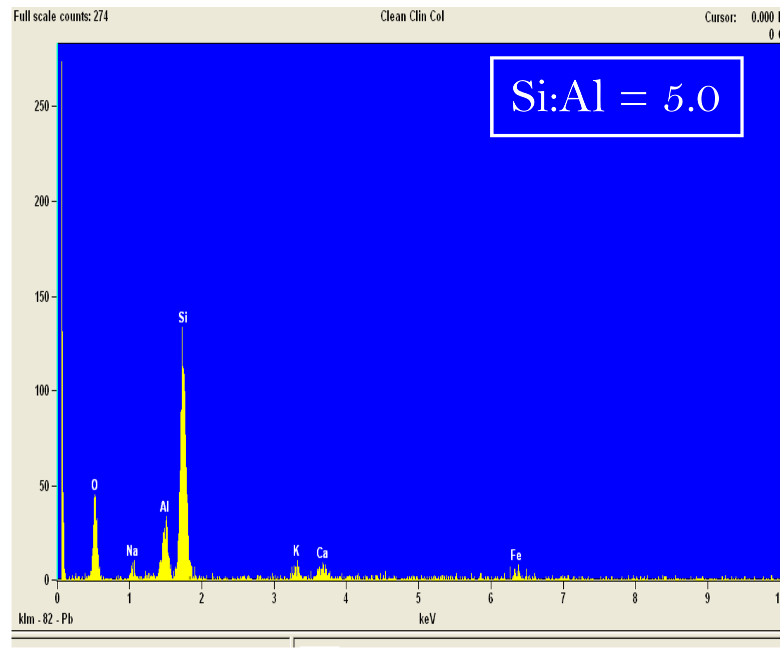
Natural Clinoptilolite Zeolite

SEM Analysis



Clinoptilolite crystal clusters

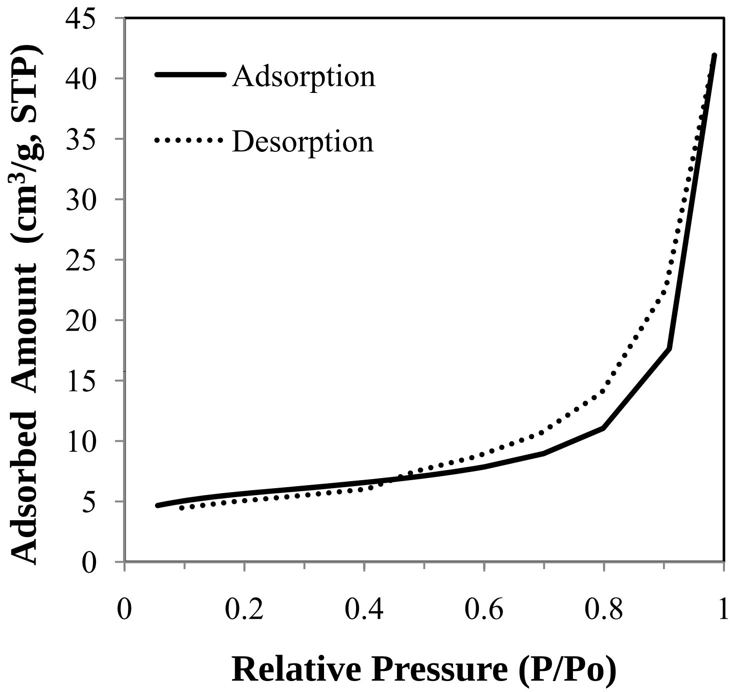
EDS Analysis

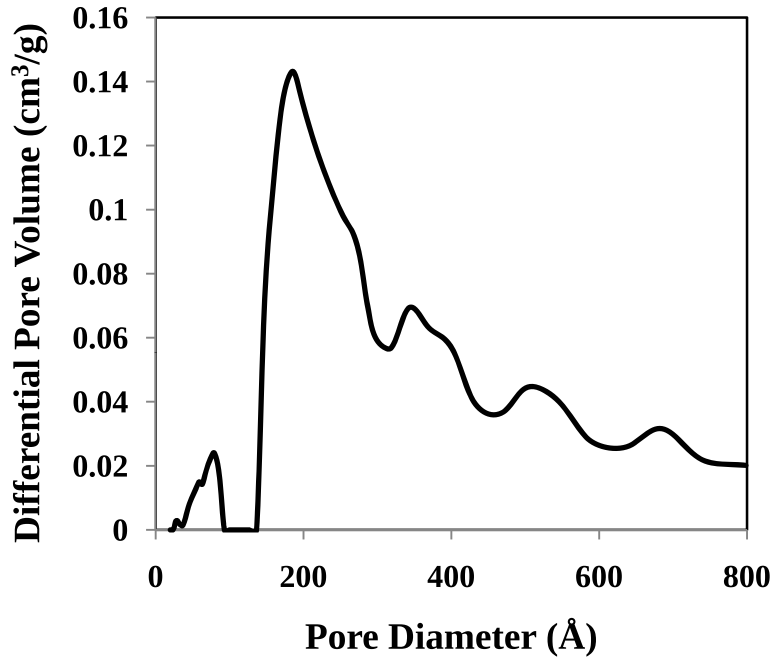


$(Na, K, Ca)_{2-3}Al_3(Al, Si)_2Si_{13}O_{36}-12H_2O$

Natural Clinoptilolite Zeolite

N_2 adsorption analysis

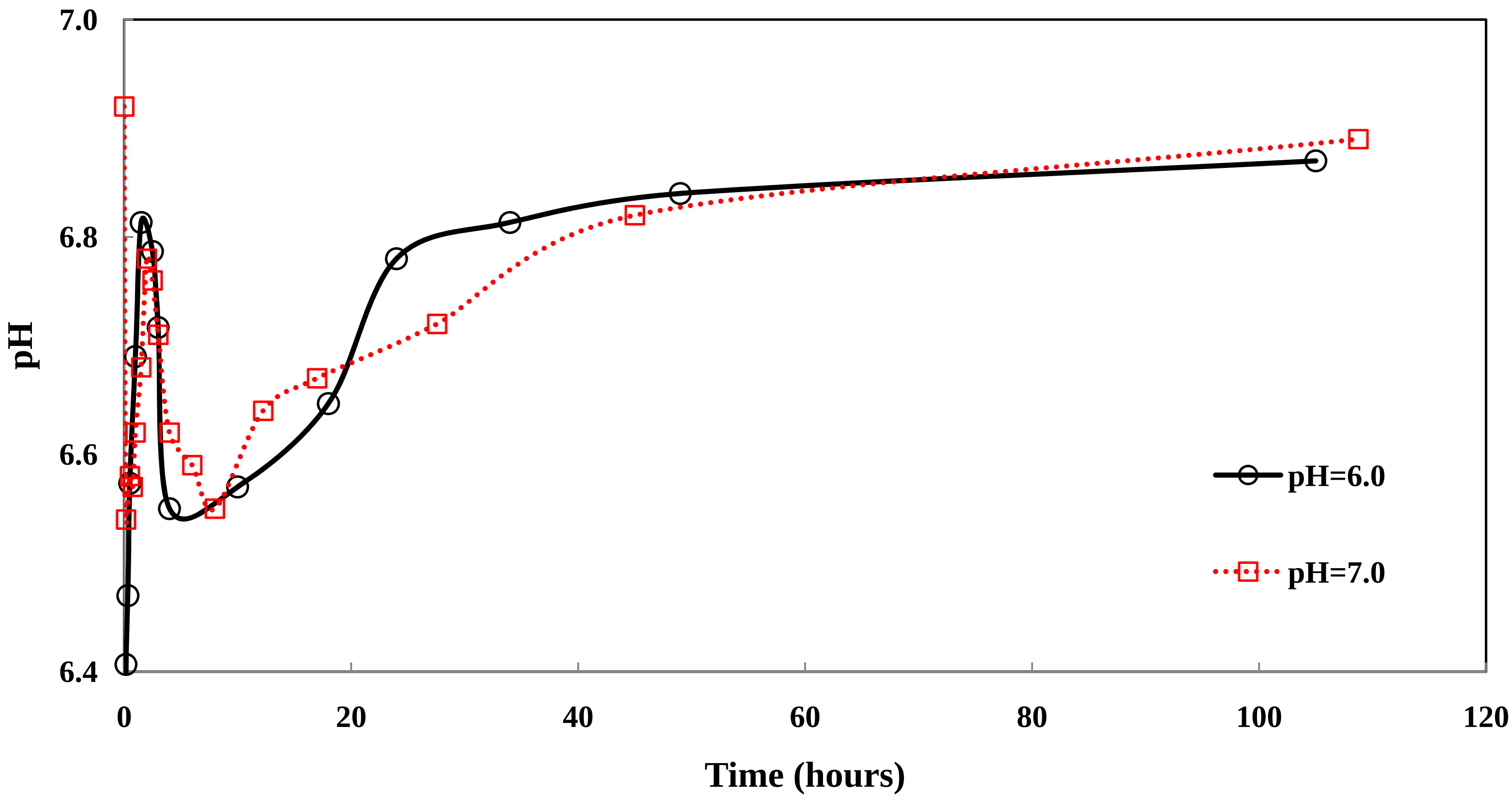




BET surface area = 18.0 m^2/g; Average pore size = 166 Å

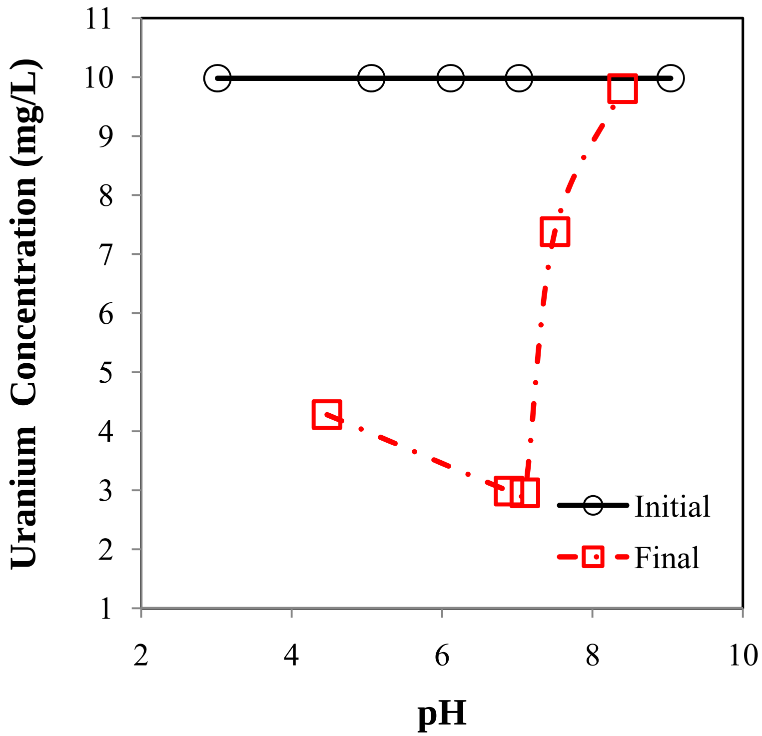
Uranium Adsorption Results

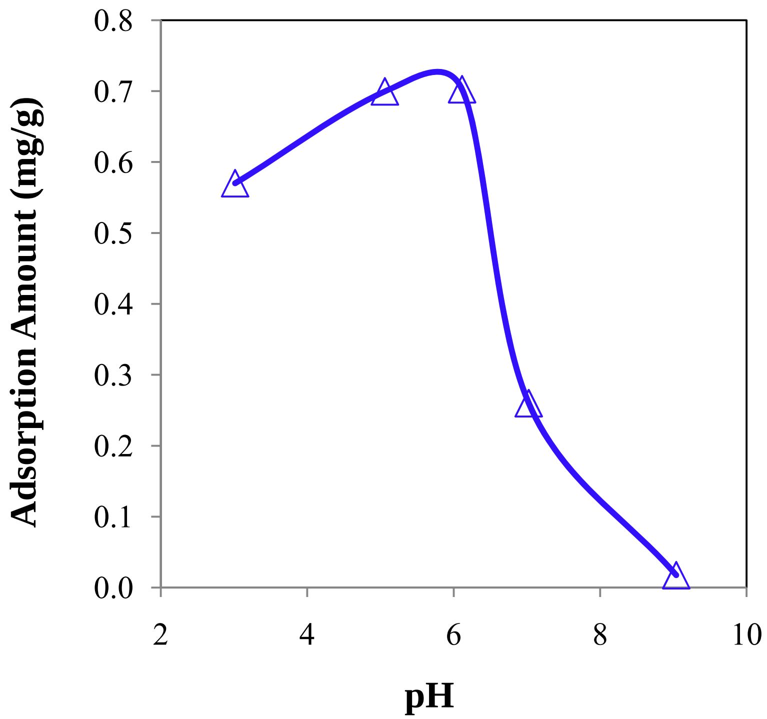
pH Behavior



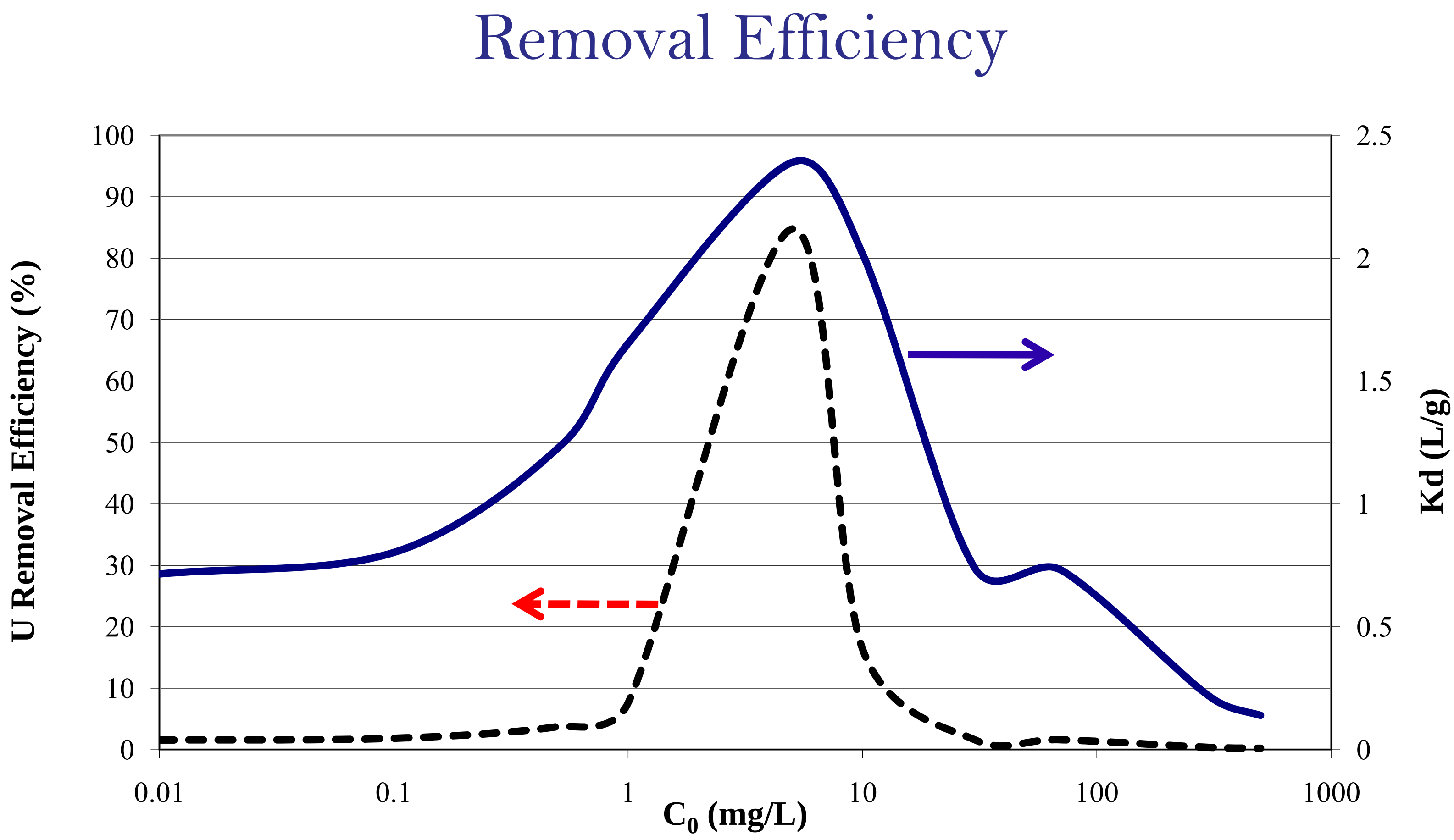
Uranium Adsorption Results

Effect of pH on Uranium Uptake





Uranium Adsorption Results



Uranium Adsorption Results

Data Analysis: Adsorption Equilibrium Models

$$q = KC_e^{\frac{1}{n}}$$

Freundlich

$$q = \frac{q_m bC_e}{1 + bC_e}$$

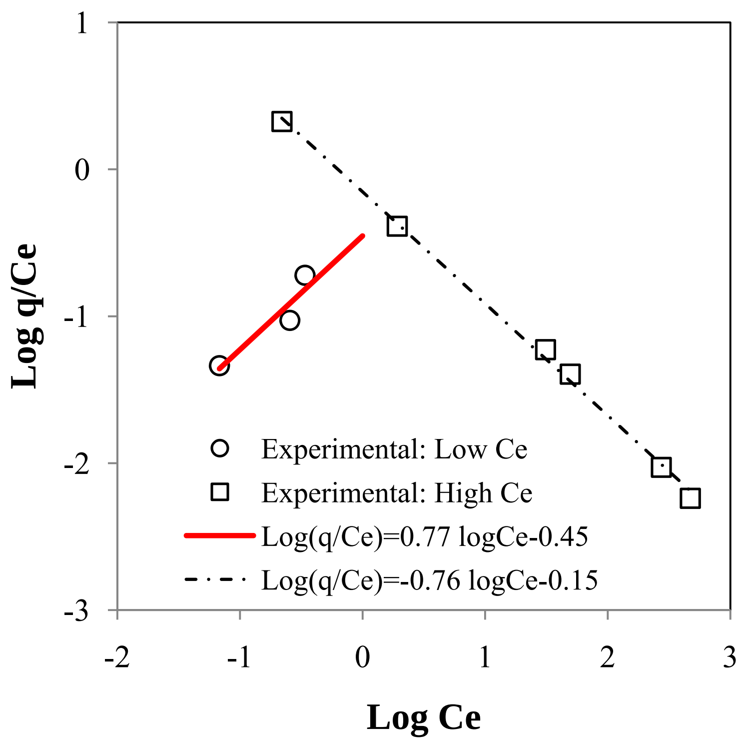
Langmuir

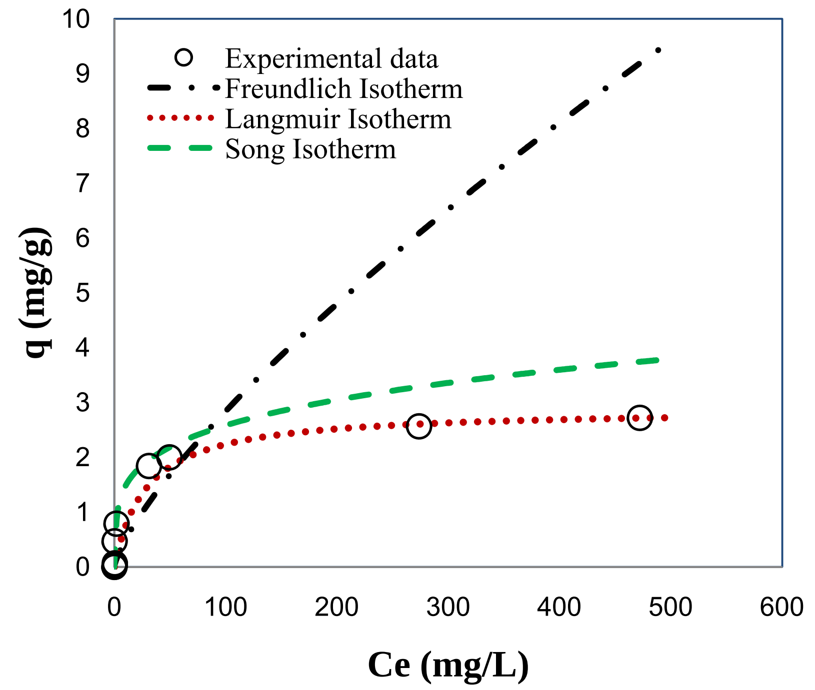
$$q = K\left(1 + \beta C_e^2\right)^{(n-1)/2} C_e$$

Song

Uranium Adsorption Results

Adsorption Equilibrium Models





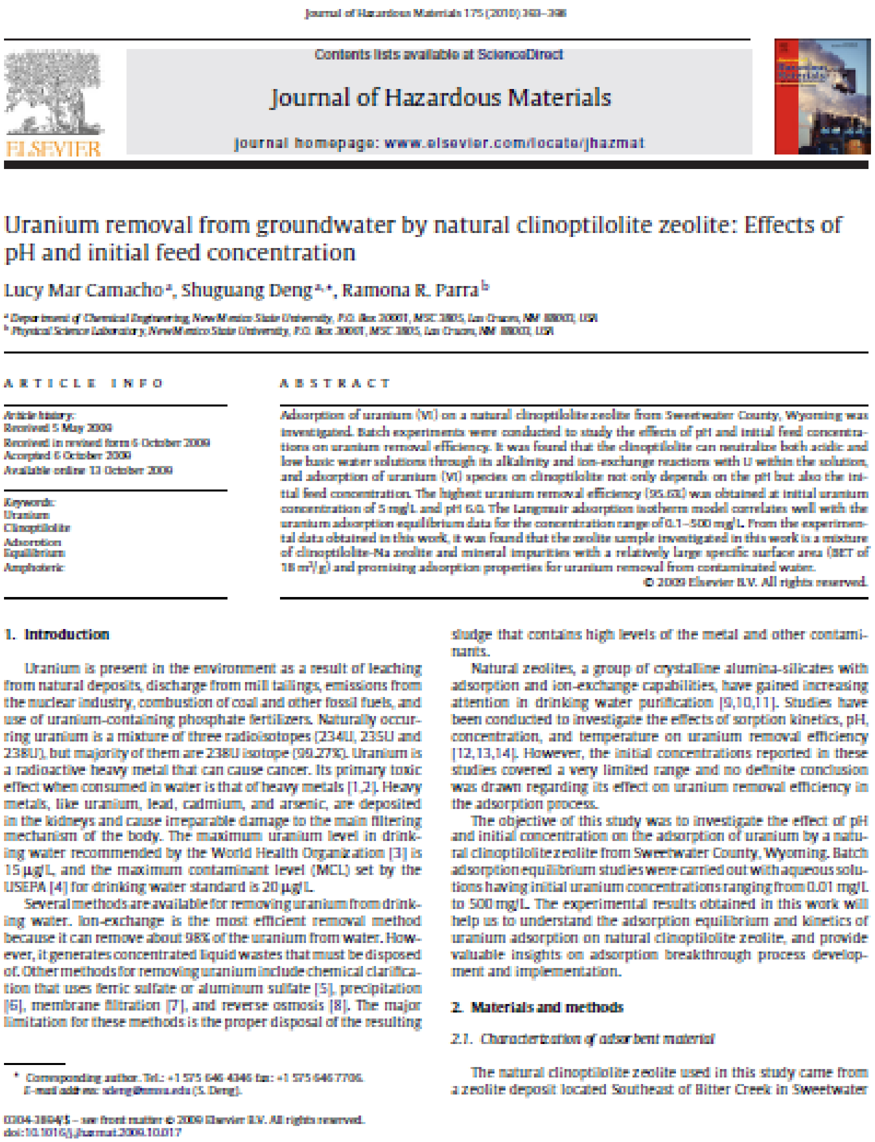
Uranium Adsorption Results

Model	Parameter	Value
Freundlich	K (L/g)	2.71E-3
	n	1.287
	R^2	0.702
Langmuir	B (mg/g)	1.43E-3
	Q_m (L/mg)	1.045
	R^2	0.997
Song	K (L/g)	0.6357
	β $(mg/L)^{-2}$	0.4533
	n	0.239
	R^2 (Low C_e) R^2 (High C_e)	0.958 0.997

Summary on Uranium Removal

- The natural clinoptilolite zeolite can adsorb uranium in water, it has an adsorption distribution coefficient of 2.12 ml/g and a removal efficiency of 95.6% at an uranium concentration of 5 mg/L and pH of 6.0.
- Uranium adsorption depends on the pH and the initial concentration.
- The Langmuir isotherm model fits the isotherm data well.

Publications on Uranium Removal



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Uranium removal from groundwater by natural clinoptilolite zeolite: Effects of pH and initial feed concentration

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ABSTRACT

Adsorption of uranium (VI) on a natural clinoptilolite zeolite from Sweetwater County, Wyoming was investigated. Batch experiments were conducted to study the effects of pH and initial feed concentrations on uranium removal efficiency. It was found that the clinoptilolite can neutralize both acidic and low basic water solutions through its alkalinity and ion-exchange reactions with U within the solution, and adsorption of uranium (VI) species on clinoptilolite not only depends on the pH but also the initial feed concentration. The highest uranium removal efficiency (95.6%) was obtained at initial uranium concentration of 5 mg/L and pH 6.0. The Langmuir adsorption isotherm model correlates well with the uranium adsorption equilibrium data for the concentration range of 0.1–500 mg/L. From the experimental data obtained in this work, it was found that the zeolite sample investigated in this work is a mixture of clinoptilolite-Na zeolite and mineral impurities with a relatively large specific surface area (BET of 18 m^2/g) and promising adsorption properties for uranium removal from contaminated water.

1. Introduction

Uranium is present in the environment as a result of leaching from natural deposits, discharge from mill tailings, emissions from the nuclear industry, combustion of coal and other fossil fuels, and use of uranium-containing phosphate fertilizers. Naturally occurring uranium is a mixture of three radioisotopes (234U, 235U and 238U), but majority of them are 238U isotope (99.27%). Uranium is a radioactive heavy metal that can cause cancer. Its primary toxic effect when consumed in water is that of heavy metals [1,2]. Heavy metals, like uranium, lead, cadmium, and arsenic, are deposited in the kidneys and cause irreparable damage to the main filtering mechanism of the body. The maximum uranium level in drinking water recommended by the World Health Organization [3] is 15 μg/L, and the maximum contaminant level (MCL) set by the USEPA [4] for drinking water standard is 20 μg/L.

Several methods are available for removing uranium from drinking water. Ion-exchange is the most efficient removal method because it can remove about 98% of the uranium from water. However, it generates concentrated liquid wastes that must be disposed of. Other methods for removing uranium include chemical clarification that uses ferric sulfate or aluminum sulfate [5], precipitation [6], membrane filtration [7], and reverse osmosis [8]. The major limitation for these methods is the proper disposal of the resulting sludge that contains high levels of the metal and other contaminants.

Natural zeolites, a group of crystalline alumina-silicates with adsorption and ion-exchange capabilities, have gained increasing attention in drinking water purification [9,10,11]. Studies have been conducted to investigate the effects of sorption kinetics, pH, concentration, and temperature on uranium removal efficiency [12,13,14]. However, the initial concentrations reported in these studies covered a very limited range and no definite conclusion was drawn regarding its effect on uranium removal efficiency in the adsorption process.

The objective of this study was to investigate the effect of pH and initial concentration on the adsorption of uranium by a natural clinoptilolite zeolite from Sweetwater County, Wyoming. Batch adsorption equilibrium studies were carried out with aqueous solutions having initial uranium concentrations ranging from 0.01 mg/L to 500 mg/L. The experimental results obtained in this work will help us to understand the adsorption equilibrium and kinetics of uranium adsorption on natural clinoptilolite zeolite, and provide valuable insights on adsorption breakthrough process development and implementation.

2. Materials and methods

2.1. Characterization of adsorbent material

The natural clinoptilolite zeolite used in this study came from a zeolite deposit located Southeast of Bitter Creek in Sweetwater

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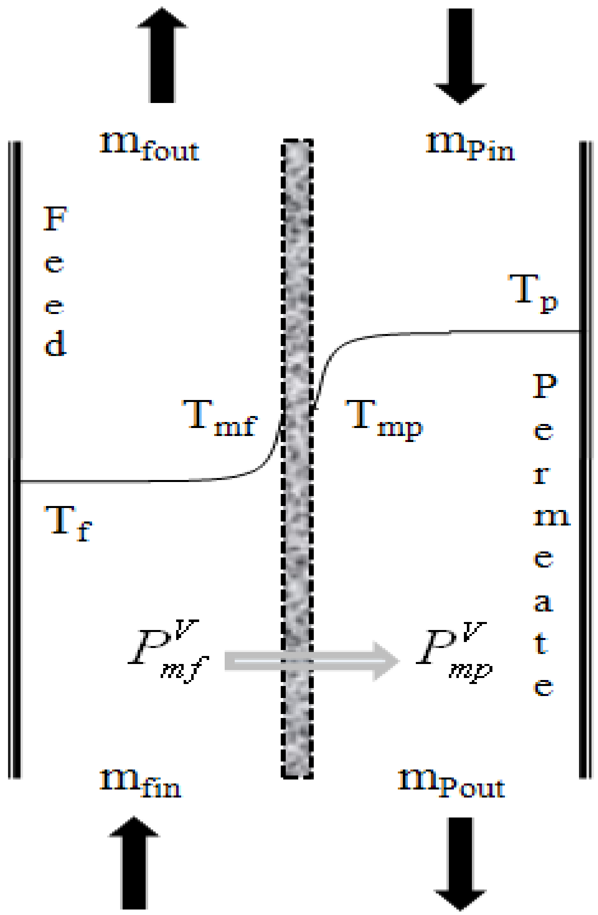
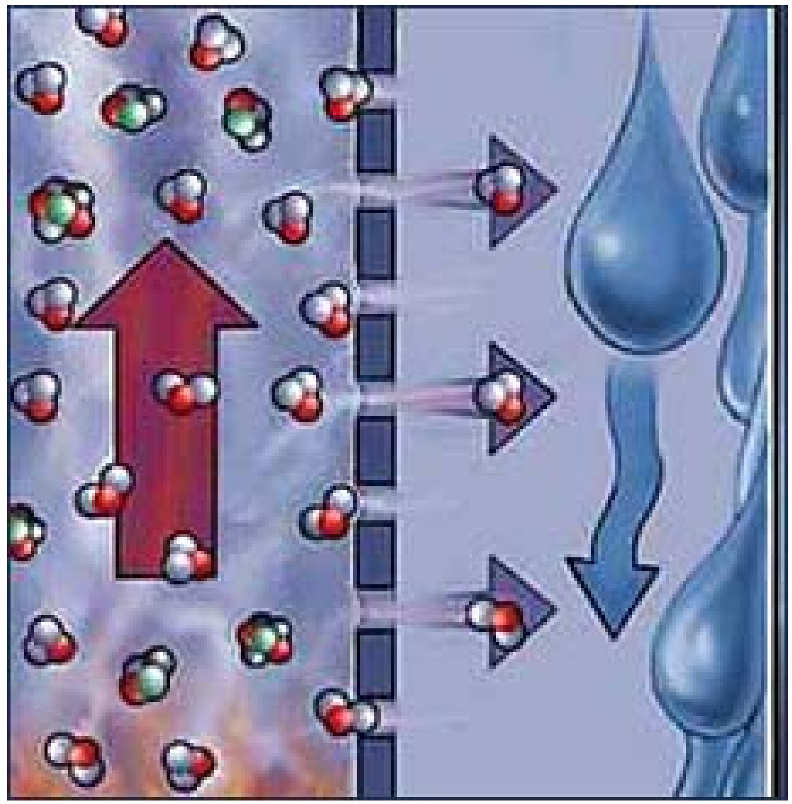
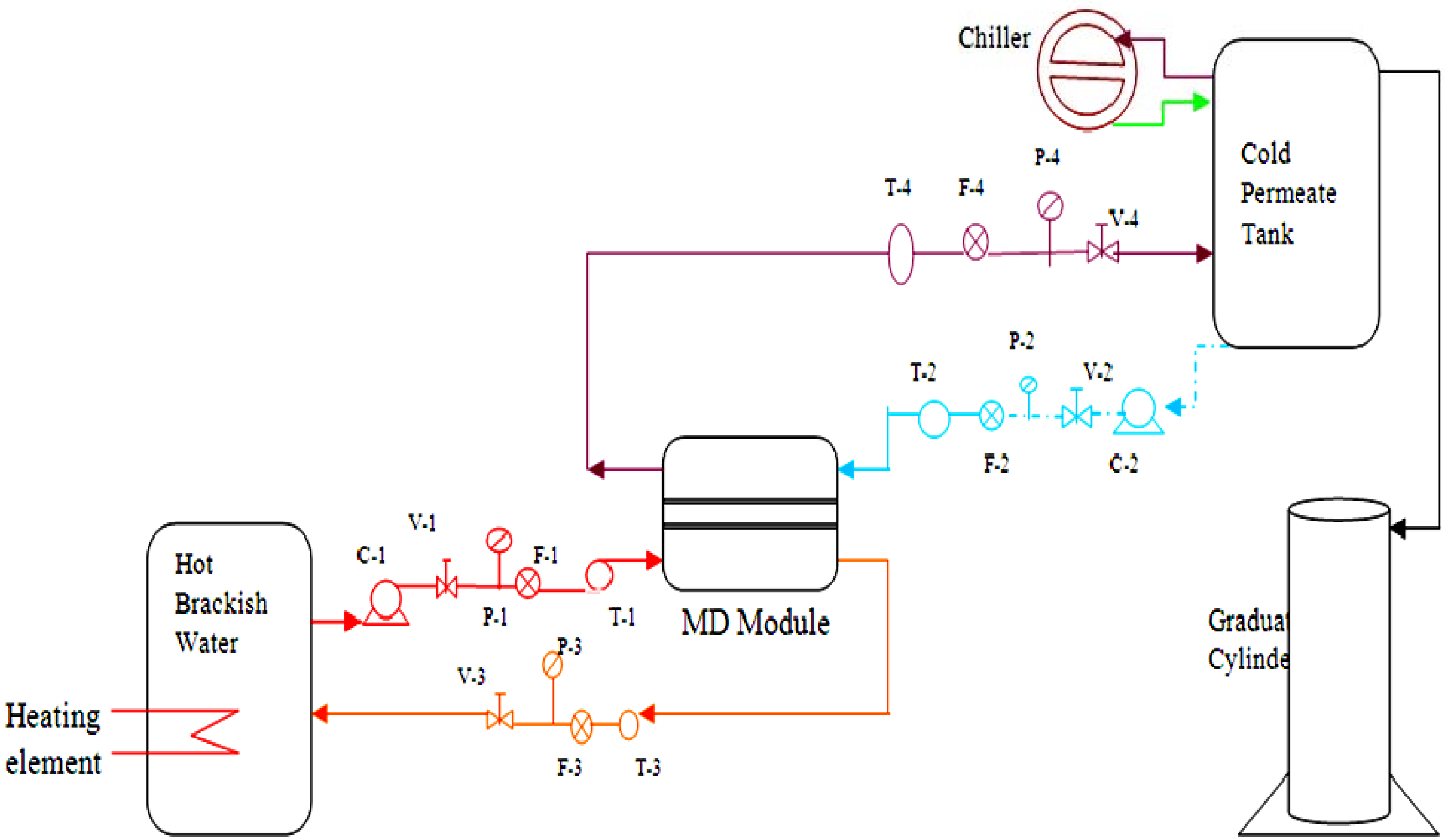
Membrane Distillation for U Removal





Membrane Distillation for U Removal



Membrane Distillation for U Removal

DCMD Apparatus at NMSU

DCMD module

Hollow Fiber Module

Membrane Distillation for U Removal

Contaminant	Feed Concentration	Product Concentration	Removal efficiency (%)
Salts	5500-6500 ppm	10-15 ppm	99.80
Uranium	300-400 ppb	<2 ppb	99.82
Arsenic	400-500 ppb	< 1 ppb	99.96
Fluoride	25 – 30 ppm	0.5-1.2 ppm	98.34

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