COMPARATIVE STUDY OF ARSENIC REMOVAL EFFICIENCY FROM WATER BY ADSORPTION AND PHOTOCATALYTIC OXIDATION WITH TITANIUM DIOXIDE

Züleyha Özlem KOCABAŞ, Yuda YÜRÜM

Faculty of Engineering and Natural Sciences, Sabancı University

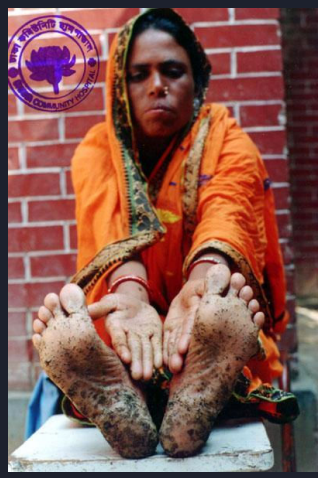
Background

- The significantly high contamination level of arsenic has been reported for many countries as India, USA, Mexico, China, Argentina and Turkey.
- Arsenic is severely harmful to the human health and long term exposure to arsenic can lead to cancer of the lungs, skin, kidney and liver.
- World Health Organization (WHO) lowered arsenic level in drinking water from 50 to 10 ppb on Jan 23, 2006*.

- Arsenic is naturally occurring element.

  Natural sources:
  - Dissolution and weathering of rocks
  - Volcanoes
  - Forest fires

  Manmade/man-affected sources:
  - Agriculture
  - Mining and industrial wastes



** http://www.wired.com/wiredscience/2008/04/science-prize-h/

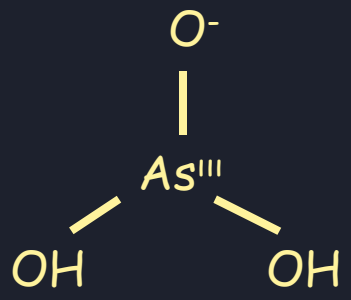
2* USEPA, Federal Register, 66 (14) (2001) 6976-7066.

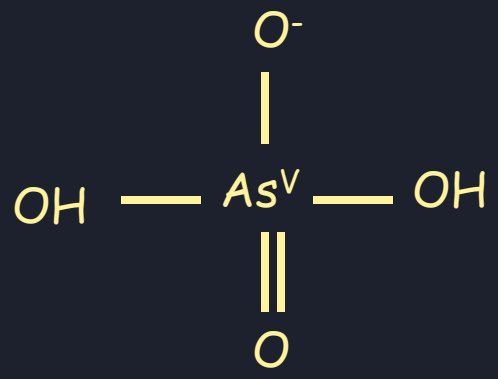
Chemistry Behind Arsenic

- In natural water, arsenic occurs both in organic and inorganic forms.
- Inorganic arsenic exists in -3, 0, +3 and +5 oxidation states in aquatic systems. The elemental state 0 and -3 are quite rare as compared to +3 and +5 oxidation states.

As (III) - As^{+3} Arsenite

As (V) - As^{+5} Arsenate





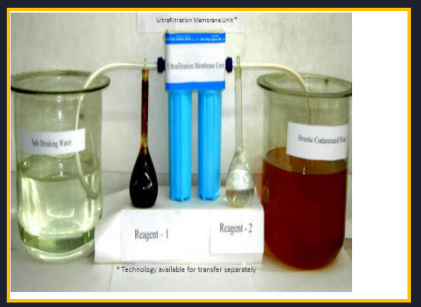
➔ As (III) has greater toxicity and mobility than As (V).

➔ Organic arsenic is detoxified by methylation process.

Inorganic arsenic is needed a well-established treatment.

Arsenic Treatment Options

- Coagulation – coprecipitation
- Ion exchange technique
- Membrane technologies
- Reverse osmosis
- Nanofiltration
- Bioremediation
- Adsorption



Objectives

- Synthesis of anatase nanoparticles for adsorption and photocatalytic oxidation processes
- Analysis of the arsenic adsorption on the surface of anatase nanoparticles since relatively few studies exist on that field
- Understanding the photocatalytic oxidation mechanism of As(III) by using anatase nanoparticles under UV illumination

Adsorbent Material- Titanium Dioxide

- ✓ It is widely used as a pigment for paints, plastics, cosmetics and toothpastes due to the its brilliant whiteness.
- ✓ It possesses a high potential for the environmental application due to the its physical and chemical stability, lower cost, nontoxicity and resistance to corrosion.
- ✓ It can be classified as three types (anatase , rutile and brookite) in terms of its crystal structure.
- ✓ Anatase has higher photocatalytic properties than rutile*.
- ✓ In this study, anatase mineral type was used as an adsorbent material.

* D. Mohan, C.U. Pittman Jr, (2007), Arsenic removal from water/wastewater using adsorbents —A critical review, *Journal of Hazardous Materials*, vol.142, pp. 1–53.

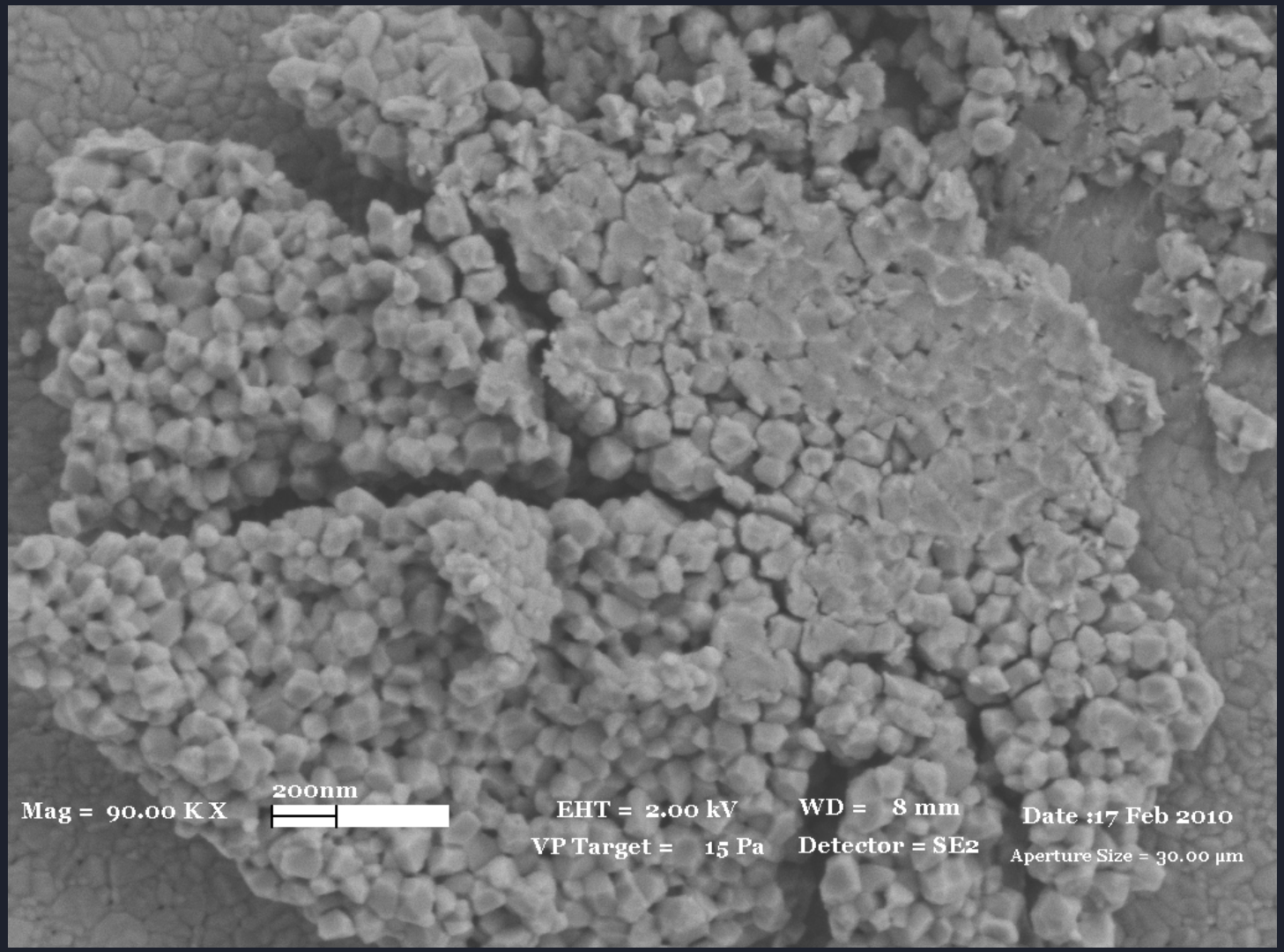
Synthesis Route of Anatase Nanoparticles

- A sol-gel method was used to synthesize the anatase nanoparticles .
- This method was selected because it creates amorphous particles, allowing us to control the crystallinity.

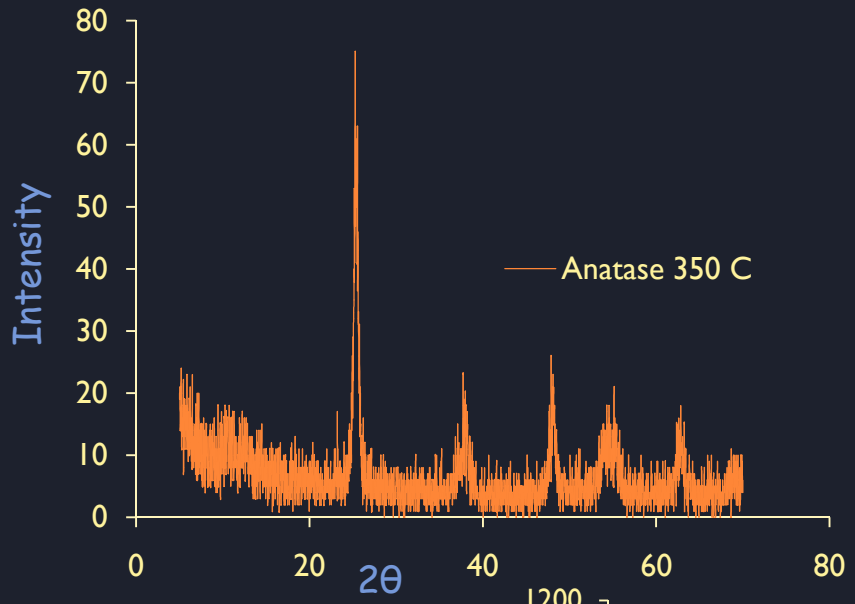
Precursor Solution		Hydrolysis Solution		Final Volume
TTIP(ml)	2-propanol (ml)	Distilled water (ml)	2-propanol (ml)	
5	15	2,5	97,5	100

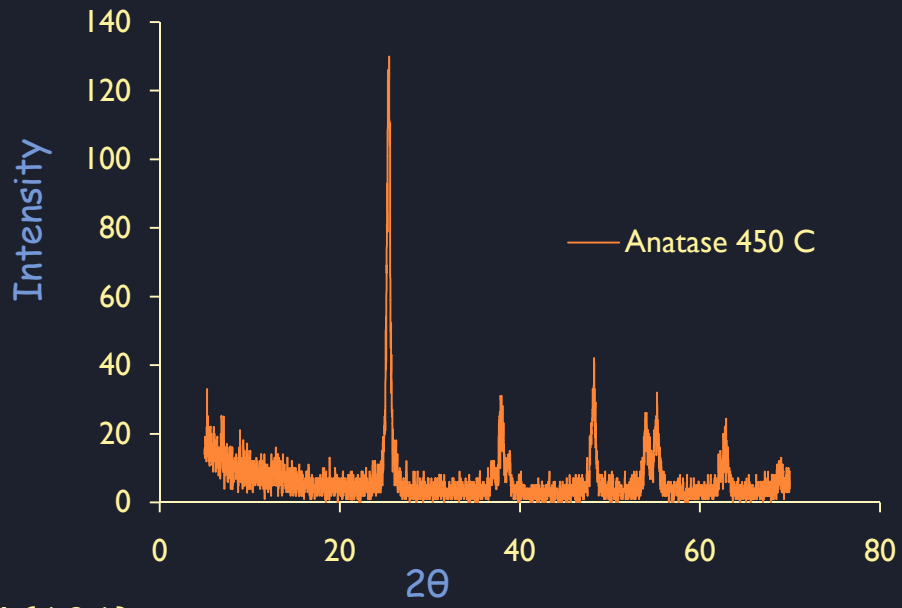
- The gel preparation process was started when the precursor and hydrolysis solutions were mixed together under continuous stirring at room temperature.
- After certain period of mixing, sample was filtrated and annealed at different temperatures for 2 h.

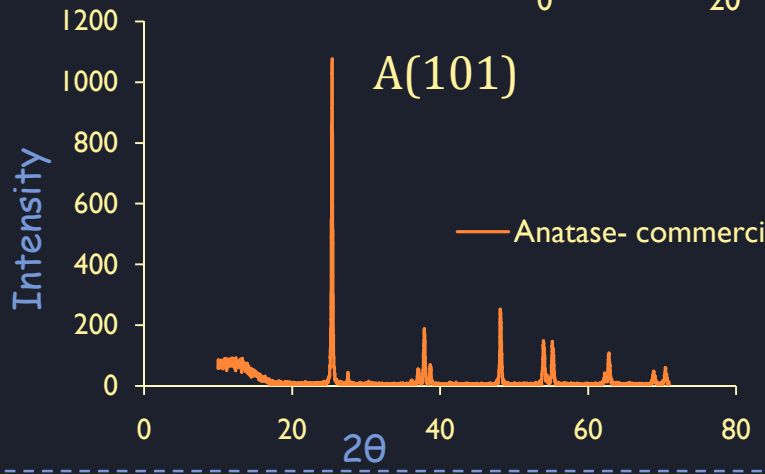
SEM Images


Mag = 90.00 K X
200nm
EHT = 2.00 kV
VP Target = 15 Pa
WD = 8 mm
Detector = SE2
Date :17 Feb 2010
Aperture Size = 30.00 µm

XRD Results

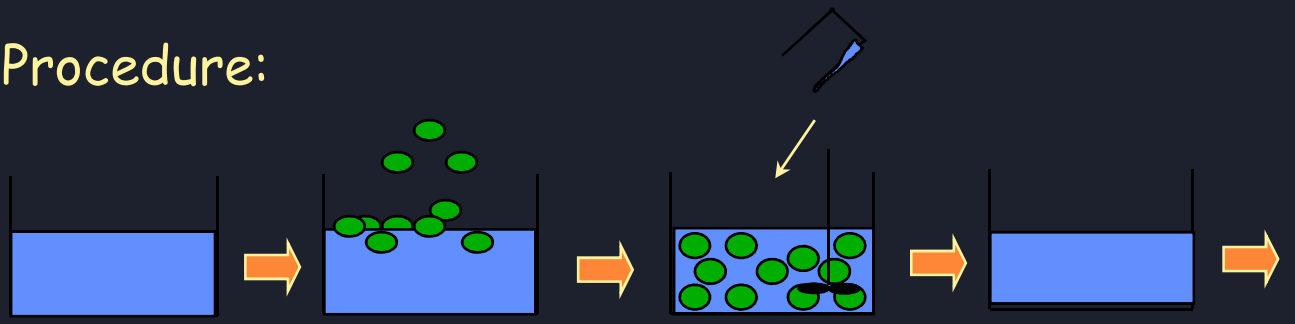

Intensity
2θ
Anatase 350 C
0
10
20
30
40
50
60
70
80
0
20
40
60
80


Intensity
2θ
Anatase 450 C
0
20
40
60
80
100
120
140
0
20
40
60
80


A(101)
Intensity
2θ
Anatase- commercial
0
200
400
600
800
1000
1200
0
20
40
60
80

Batch Adsorption Experiments

Procedure:



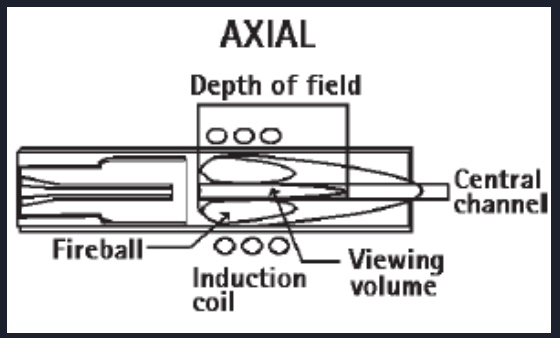
Prepare working solution - (contains arsenic species)

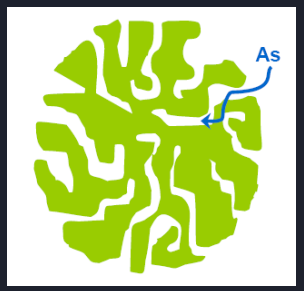
Add adsorbent material

Arrange pH with acid or base

Filtrate solution with 0,45µm syringe

Analysis of solutions with ICP-OES



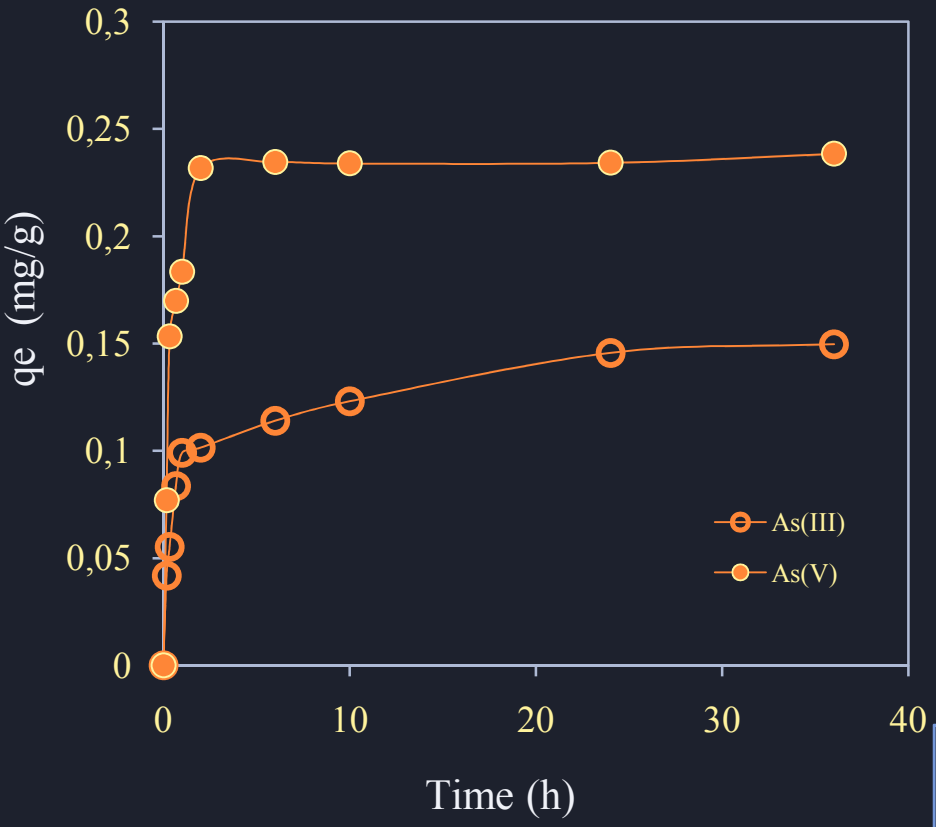


Adsorption efficiency depends on optimum;

- pH
- Contact time
- Experiment temperature
- Adsorbent amount
- Initial arsenic concentration

Effect of Contact Time

$$q_e = \frac{C_{o-} C_e}{X}$$



- Arsenic uptake (q_e) increases with increasing contact time until the state of equilibrium is reached due to saturation of adsorbent's active sites.

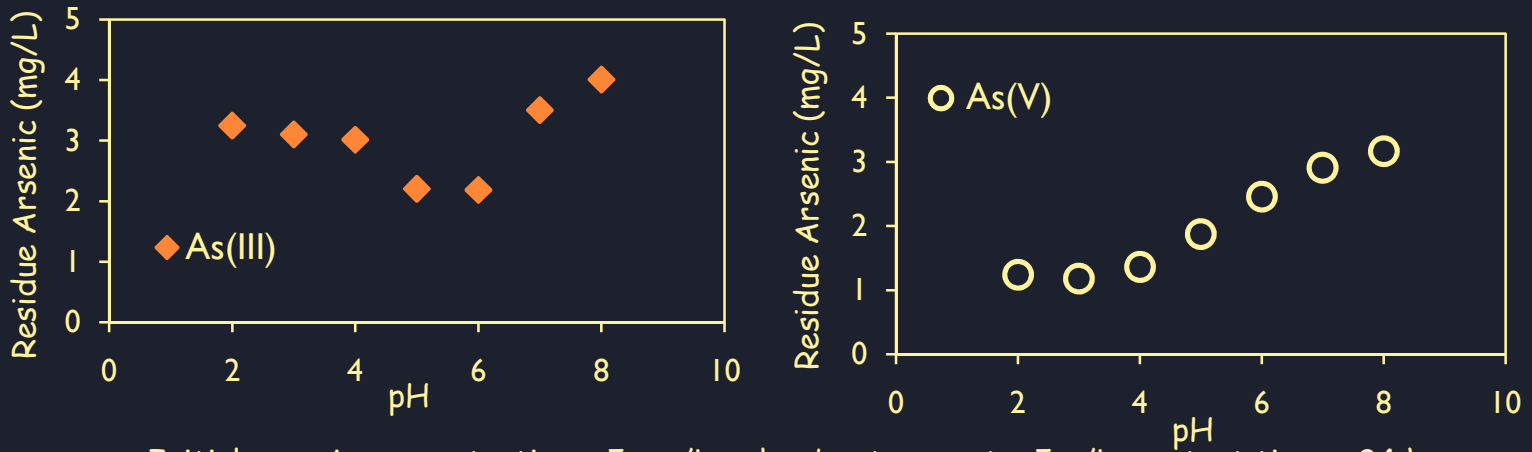
Over 81% of the arsenate is taken up within 60 min exposure and maximum 94.7% arsenate have been removed within 2 hours reaction time by anatase nanoparticles.

- The maximum 56% of arsenite have been taken up within 36 h.

Sorption Kinetics

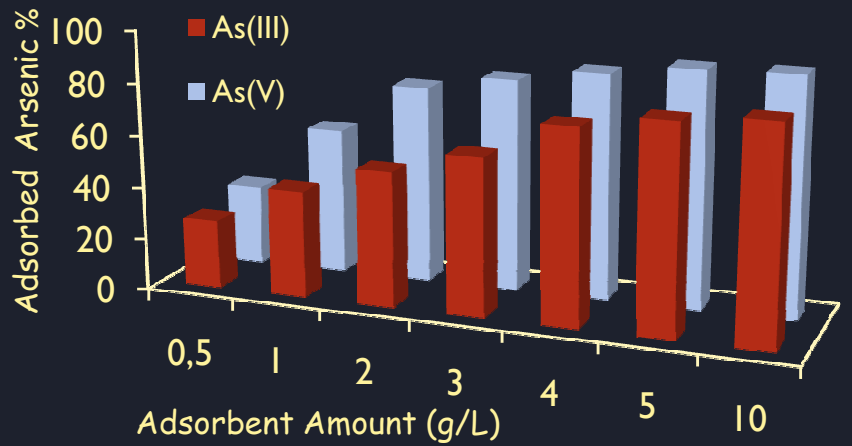
Kinetic Models	Parameters	As(III)	As(V)
Pseudo-first order:	k_1 (h^{-1})	0.032	0.024
$\log(q_e - q_t) = \log q_e - k_1 t$	q_e (mg/g)	0.338	0.283
	R^2	0.941	0.470
Pseudo-second order:	k_2 (g/mg h)	6.711	18.08
$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	q_e (mg/g)	0.152	0.239
	R^2	0.997	0.999
Interparticle diffusion:	k_p (mg/g $h^{1/2}$)	0.016	0.019
$q_t = k_p t^{1/2} + C$	C (mg/g	0.063	0.151
	R^2	0.810	0.483

Effect of pH

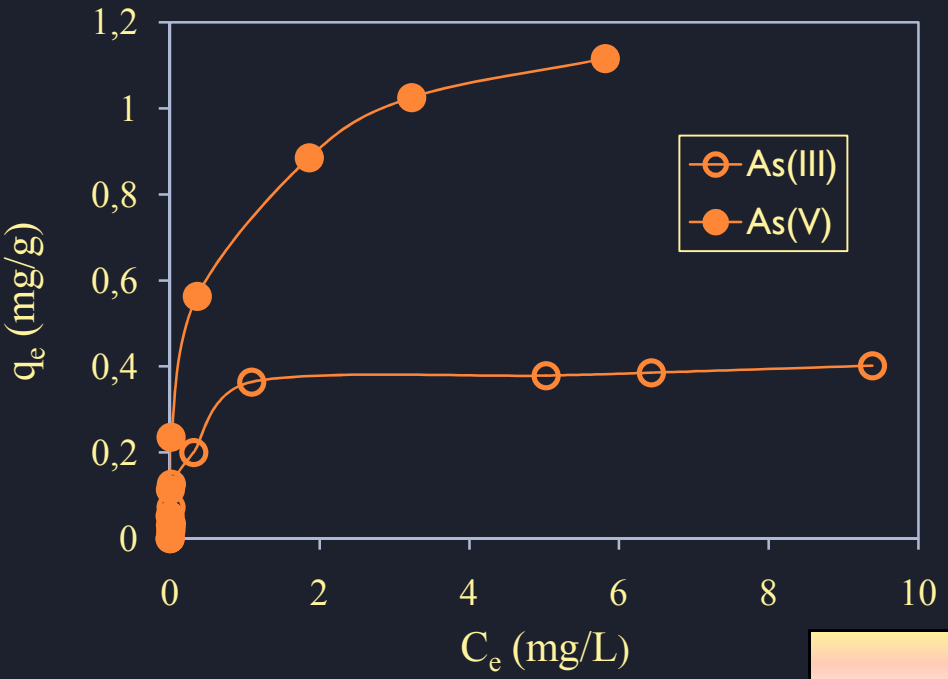


Initial arsenic concentration = 5 mg/L adsorbent amount = 5 g/L, contact time = 24 h

Effect of Adsorbent Amount



Adsorption Isotherms



❖ Comparasion of As(III) adsorption potential of anatase nanoparticles with other adsorbents

Name of Adsorbent	Adsorption capacity (mg g^{-1})
Iron oxide sand	0.029
Activated alumina	0.1803
Red mud	0.66
Iron oxide impregnated activated alumina	0.734

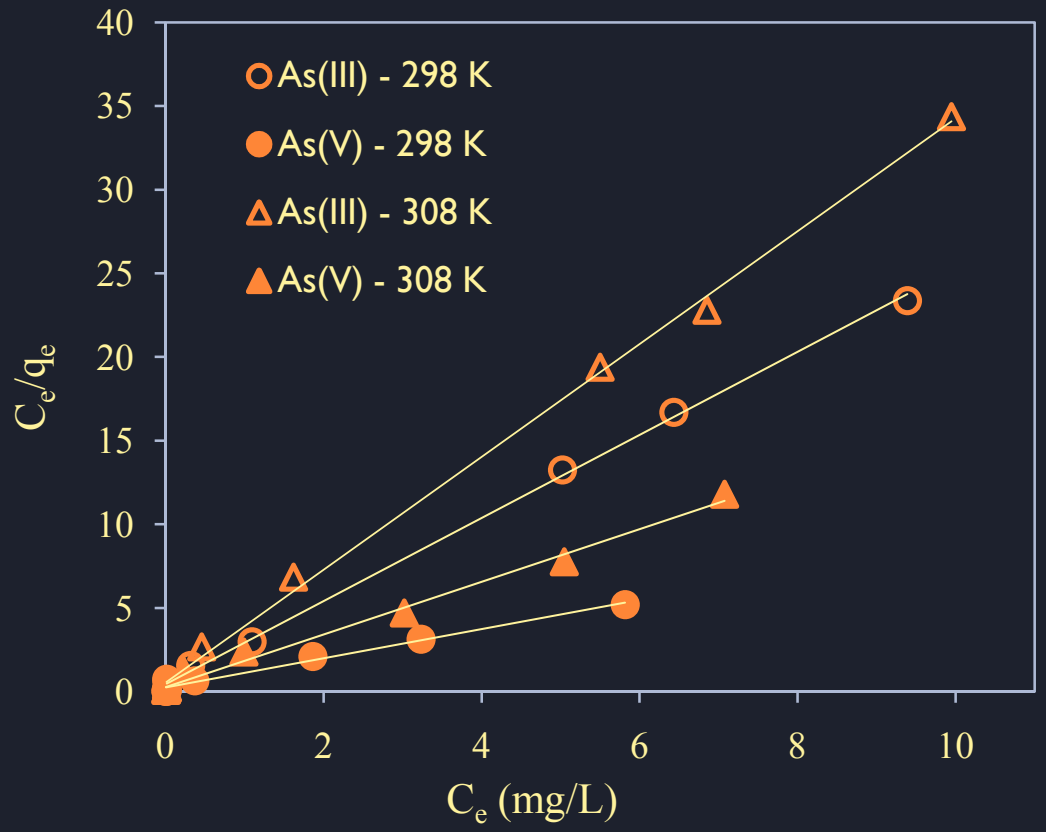
$$\frac{C_e}{q_e} = \frac{1}{q_{max}\, b} + \frac{C_e}{q_{max}}$$

$$Ln\ q_e = Ln\ K_f + \frac{1}{n} Ln\ C_e$$

	Langmuir Constants			Freundlich Constants		
anatase nanoparticles	R^2	q_{max} (mg/g)	b (1/mg)	R^2	K_f	n_f
As(III)	0.998	0.403	5.503	0.801	0.231	2.898
As(V)	0.982	1.145	3.460	0.960	2.081	0.707

* S. Ayoob et al. (2007), Performance evaluation of modified calcined bauxite in the sorptive removal of arsenic(III) from aqueous environment, Colloids and surfaces A, 293, 247-254.

Free Energy of Adsorption

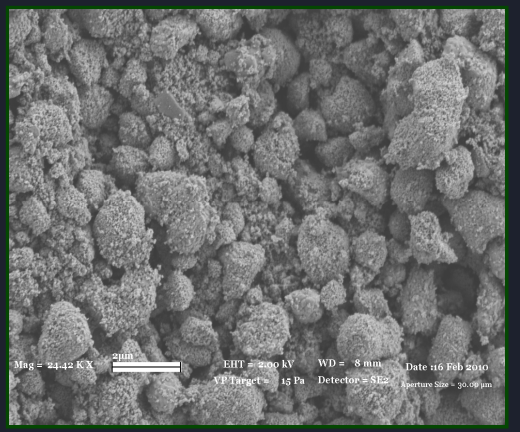


$$\Delta G = -RT \ln(K_f * 1000)$$

- The calculated free energy values are -13.48 kj/mol, -16.25 kj/mol for As(III) and As(V) at 298 K.
- The negative free energy values indicate the feasibility of the process and the spontaneous nature of adsorption.

Photocatalytic Oxidation of Arsenite

- Anatase is the widely used photocatalyst due to its strong oxidizing power and favorable band gap energy.
- Photocatalysis can rapidly oxidize arsenite (As(III)) to less toxic arsenate (As(V)) by using following mechanism*;

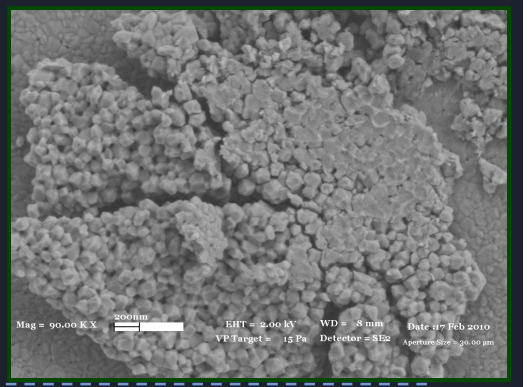


➔ Generation charge carriers and photoxidants

$$TiO_2 + hv \rightarrow TiO_2(e_{cb}^- + h_{vb}^+) \quad (1)$$

$$e_{cb}^- + O_2 \rightarrow O_2^{\cdot -} \quad (2)$$

$$h_{vb}^+ + OH^- \rightarrow HO^{\cdot} \quad (3)$$



➔ Arsenic(III) oxidation

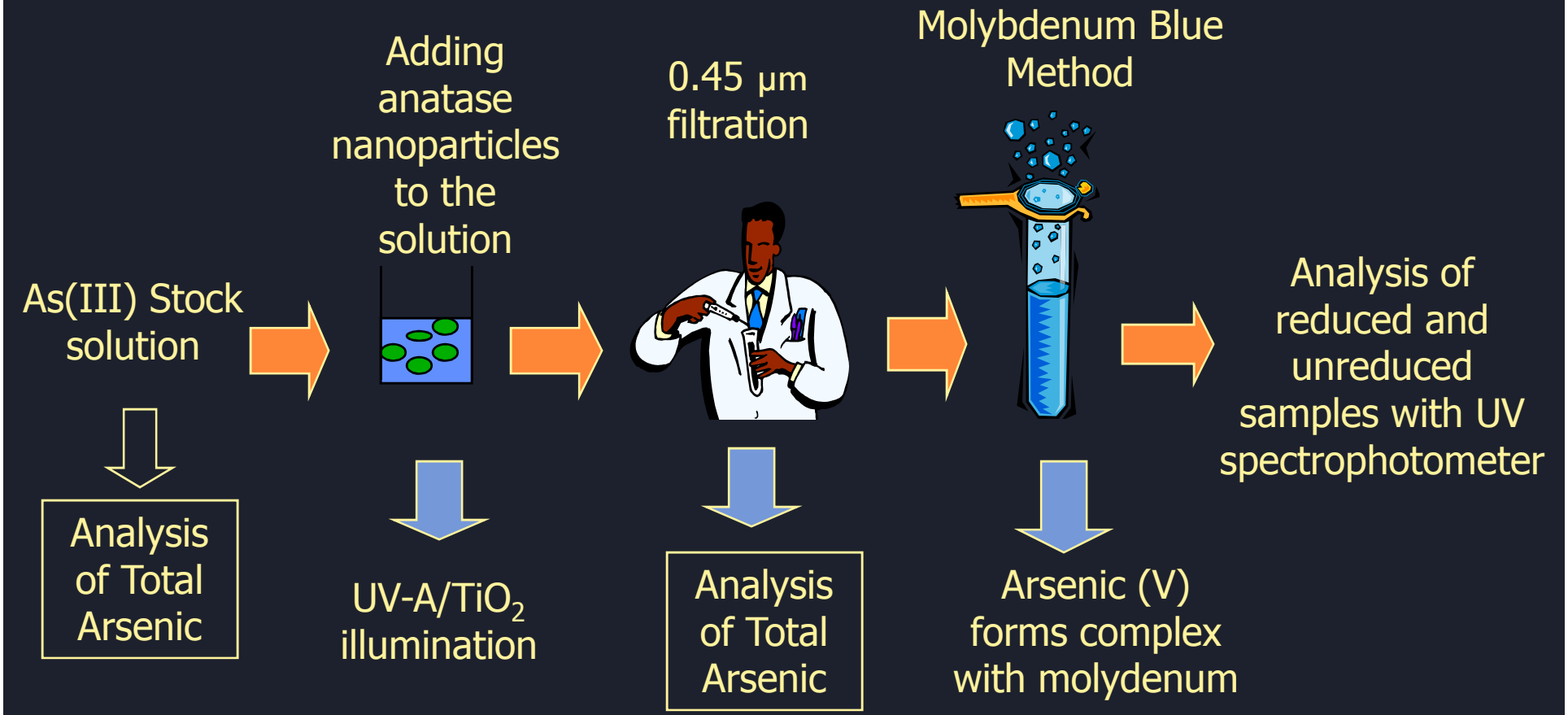
$$As(III) + HO^{\cdot} \rightarrow As(IV) + OH^- \quad (4)$$

$$As(III) + O_2^{\cdot -} \rightarrow 2H^+ \rightarrow As(IV) + H_2O_2 \quad (5)$$

$$As(IV) + O_2 \rightarrow As(V) + O_2^{\cdot -} \quad (6)$$

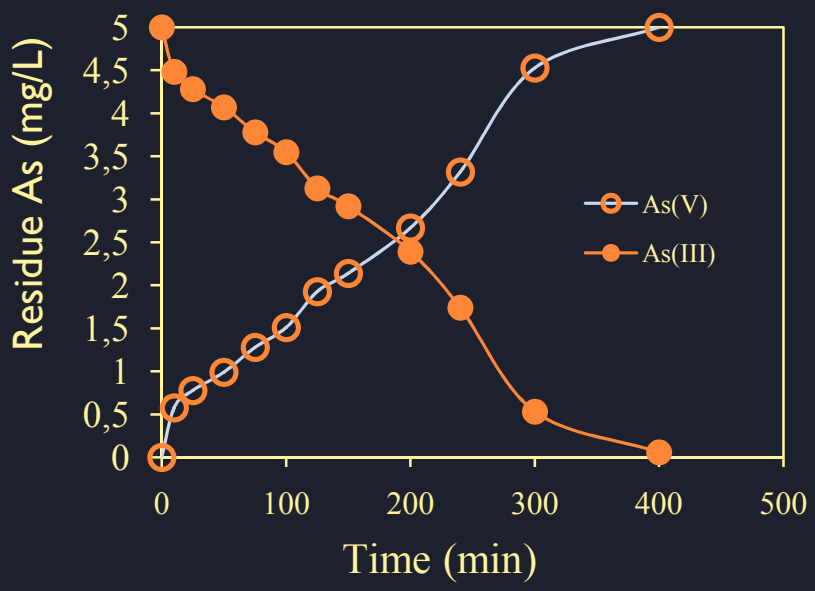
* Fu-Shen Zhang, Hideaki Itoh, (2006), Photocatalytic oxidation and removal of arsenite from water using slag-iron oxide-Tio2 adsorbent, Chemosphere 65, 125-131.

Photocatalytic Oxidation Experiments

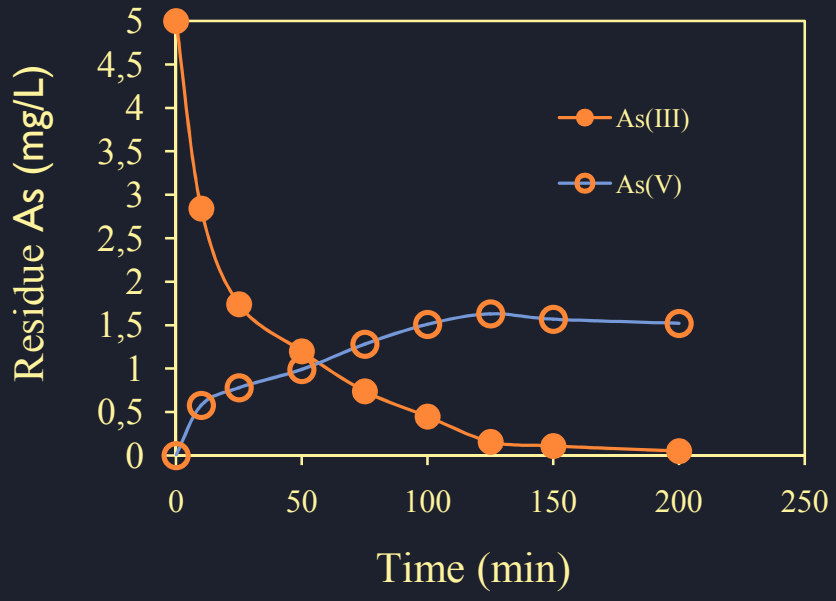


Effect of Illumination Time on Arsenic Removal

UV light only



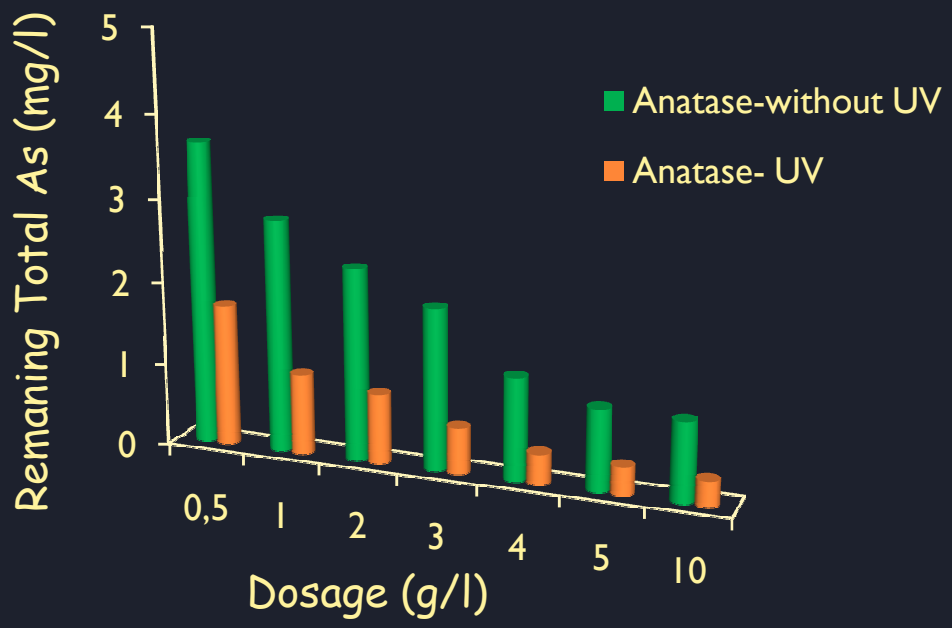
TiO_2 with UV light



- The effect of illumination time on arsenite oxidation was examined at an initial arsenite concentration of 5 mg/l and adsorbent amount 5 g/l at pH 4.

- Arsenite species could be totally oxidized to arsenate only by UV-light illumination, but the reaction rate was slower than the TiO_2 photocatalyzed reaction.

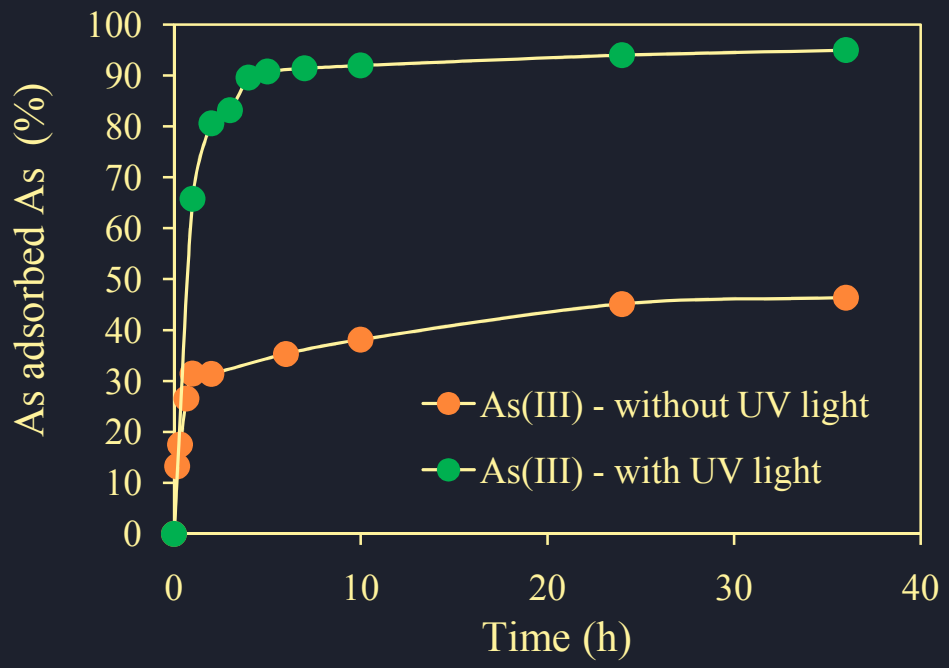
Effect of Adsorbent Amount on Total Arsenic Removal



- Experimental conditions:
  - Illumination time = 3.5 h, contact time = 4 h.
  - Without illumination, contact time = 24 h.

- Arsenic removal efficieny is greatly affected by adsorbent dosage.
- The optimum application amount of anatase nanoparticles is around 3-5 g/l for the photocatalytic experiment .

Effect of Contact Time



- Experimental conditions:
  - anatase nanoparticles dosage = 5 g/L, pH = 4, initial arsenic concentration = 5 mg/L.

- The adsorption increased linearly from the beginning and rapidly reached a plateau value within 4 h for UV-illuminated anatase nanoparticles.

Conclusion

- By using sol-gel method, anatase nanoparticles crystal was synthesized with particle size between 40-100 nm.
- Adsorption experiments were performed for anatase nanoparticles to obtain optimum pH, contact time and adsorbent amount.
- The low adsorption capacity of anatase nanoparticles from aqueous solution usually limit its application in contaminated water treatment.
- Using photocatalytic oxidation, arsenite can rapidly oxidized to arsenate, which is less toxic and mobile in aquatic environment.
- The removal capacity of As(III) from water was improved by UV- irradiation about ~90 % as compared with adsorption process of anatase nanoparticles.

Thank you for your attention..

Any Questions?

Calculation of q_e

- The amount of arsenic adsorbed per unit weight of the adsorbent was calculated by using the following equation;

$$q_e = \frac{C_{o-} C_e}{X}$$

q_e: is the concentration of the arsenic on the adsorbent (mg/g),
C_o and C_e: are the initial and the equilibrium concentrations of the arsenite or arsenate in the solution (mg/L),
X: is the dosage of the adsorbent material used (g/L).