Photocatalytic Oxidation of As^{+3} using Titania Nanoparticles for Arsenic Removal from Water

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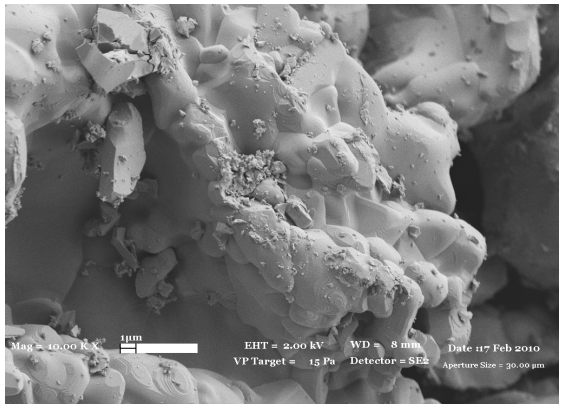
OUTLINE

- Introduction
- Arsenic treatment technologies
- Objectives
- Synthesis and characterization of titania nanoparticles
- Batch adsorption experiments
- Photocatalytic oxidation experiments
- Conclusion



Background

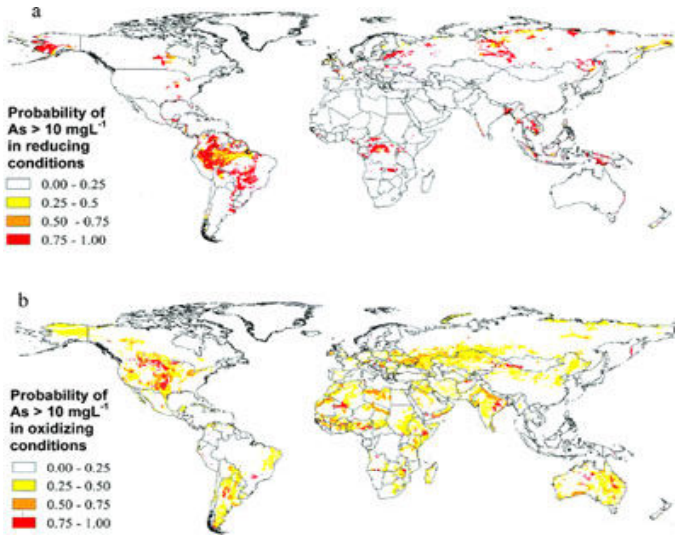
- Arsenic is naturally occurring element.

  Natural sources:

  - Dissolution and weathering of rocks
  - Volcanoes
  - Forest fires

  Manmade/man-affected sources:

  - Agriculture
  - Mining and industrial wastes



www.earthtradewater.com/.../Arsenic001.jpg

- Arsenic in water linked to skin damage or problems with circulatory system and may have an increased risk of getting cancer.
- World Health Organization (WHO) lowered arsenic level in drinking water from 50 to 10 ppb on Jan 23, 2006*.

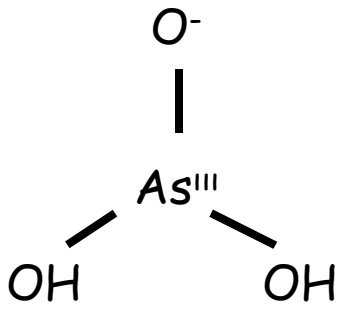
* USEPA, Federal Register, 66 (14) (2001) 6976–7066.

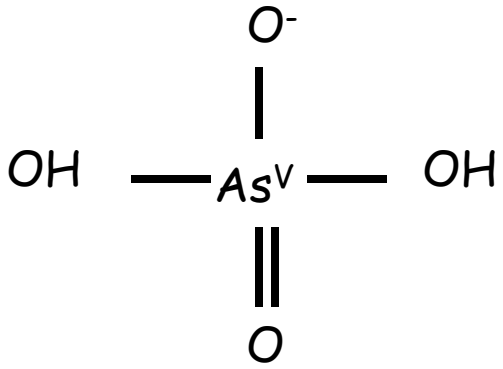
Arsenic Chemistry

- 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





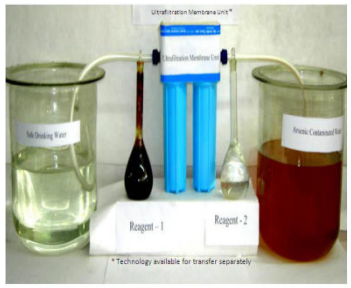
➔ As (III) has greater toxicity and mobility than As (V).

➔ 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



www.wateronline.com/.../coachella2.jpg
www.gecomwatersolutions.com/Images/
www.barc.ernet.in/technologies/images/ars.jpg

Objectives

- Synthesis of nanotitania particles for adsorption and photocatalytic oxidation processes

- Analysis of the arsenic adsorption on the surface of TiO_2 since relatively few studies exist on that field.

- Understanding the photocatalytic oxidation mechanism of As(III) by using TiO_2 under UV illumination and the adsorption behaviour of As(V) on UV illuminated-TiO_2.

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 Nanotitania

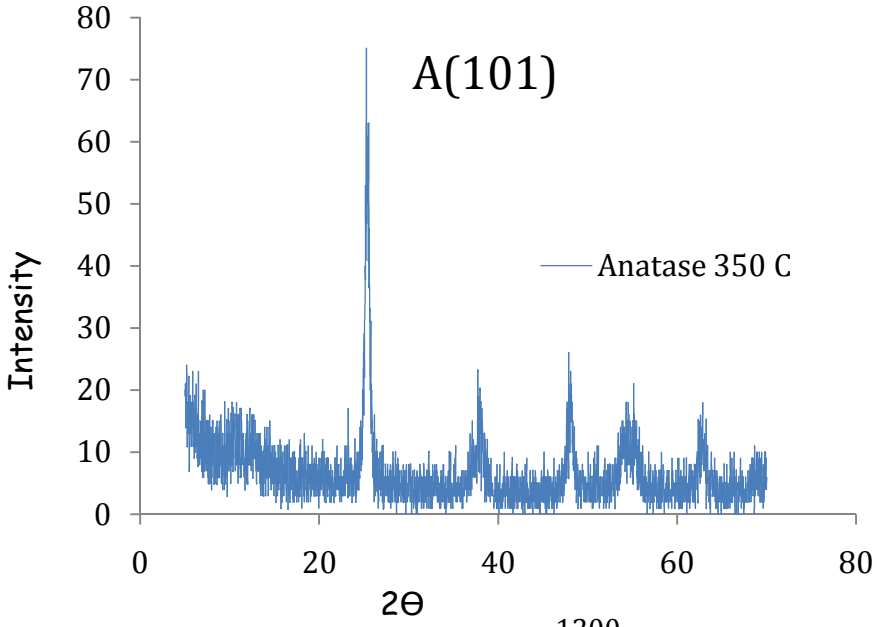
- A sol-gel method was used to synthesize the TiO_2 nanoparticles. This method was selected because it creates amorphous nanoparticles, allowing us to control the crystallinity.

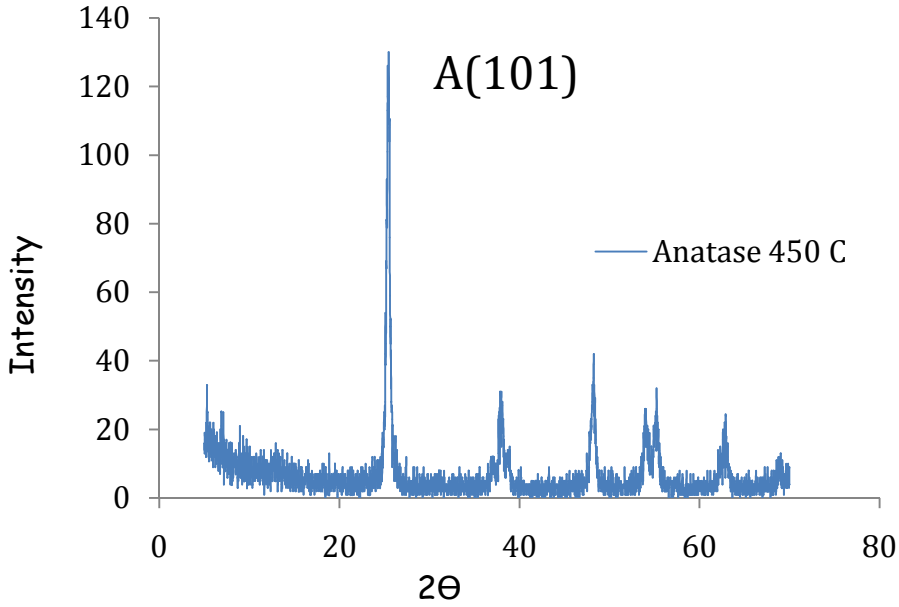
Precursor Solution		**Hydrolysis Solution**		**Final Volume**
TTIP(ml)	2-propanol (ml)	Distilled water (ml)	2-propanol (ml)	
5	15	2,5	97,5	100

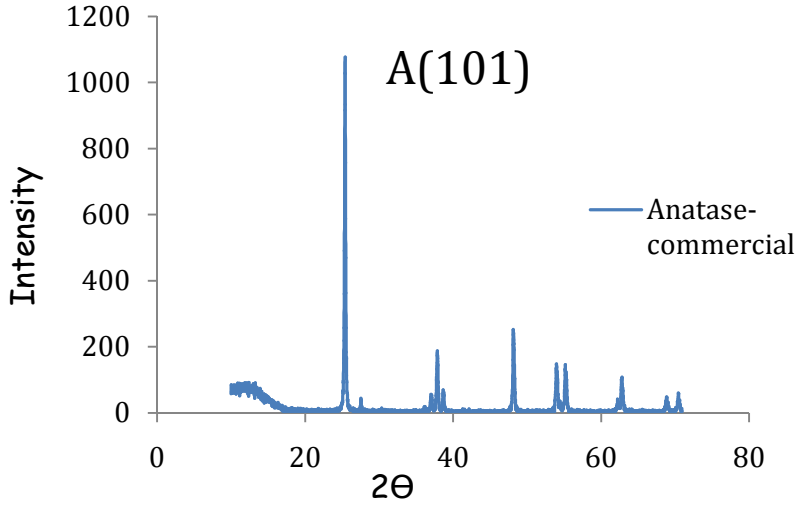
- The gel preparation process was started when the precursor and hydrolysis solutions were mixed together under continuous stirring at room temperature.
- After certain period of mixing, sample was filtrated, dried for several hours at 100 °C and annealed at different temperature for 2 h*.

* S. Mahshida, M. Askaria, M. Sasani Ghamsarib, N. Afsharc, S. Lahutic, (2009), Mixed-phase TiO_2 nanoparticles preparation using sol–gel method, Journal of Alloys and Compounds, 478, 586–589.

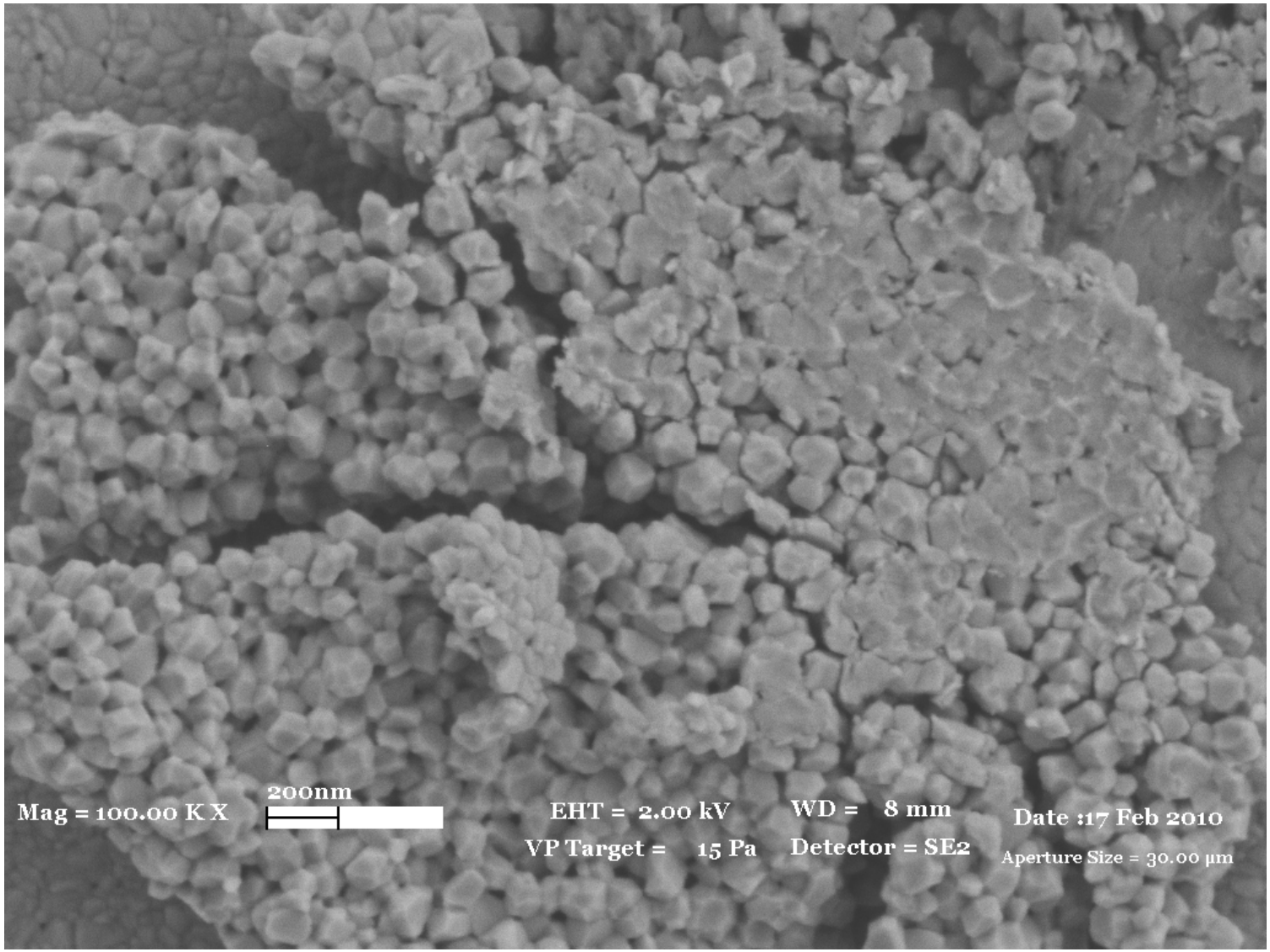
Characterization – XRD Results





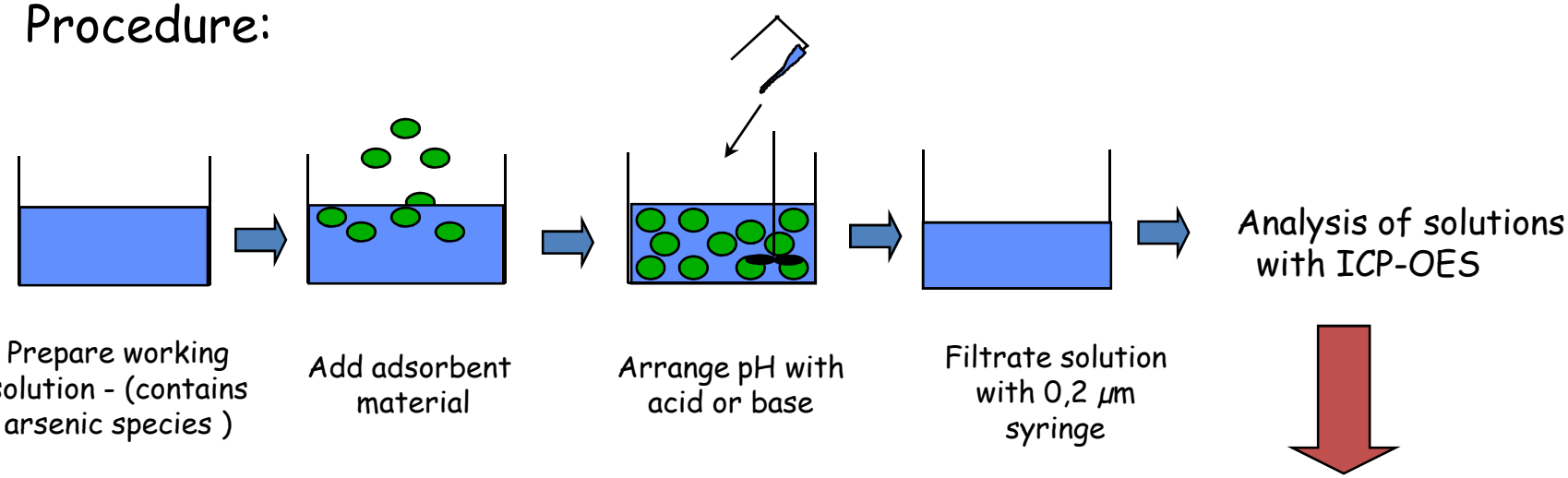


Characterization – SEM images



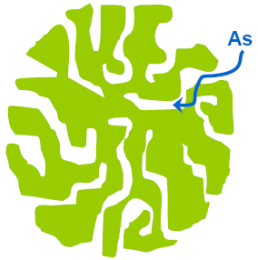
Batch Adsorption Experiment

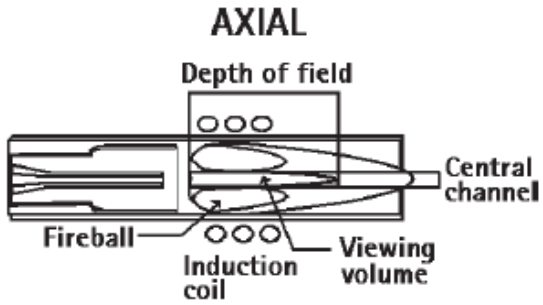
Procedure:



Adsorption efficiency depends on optimum;

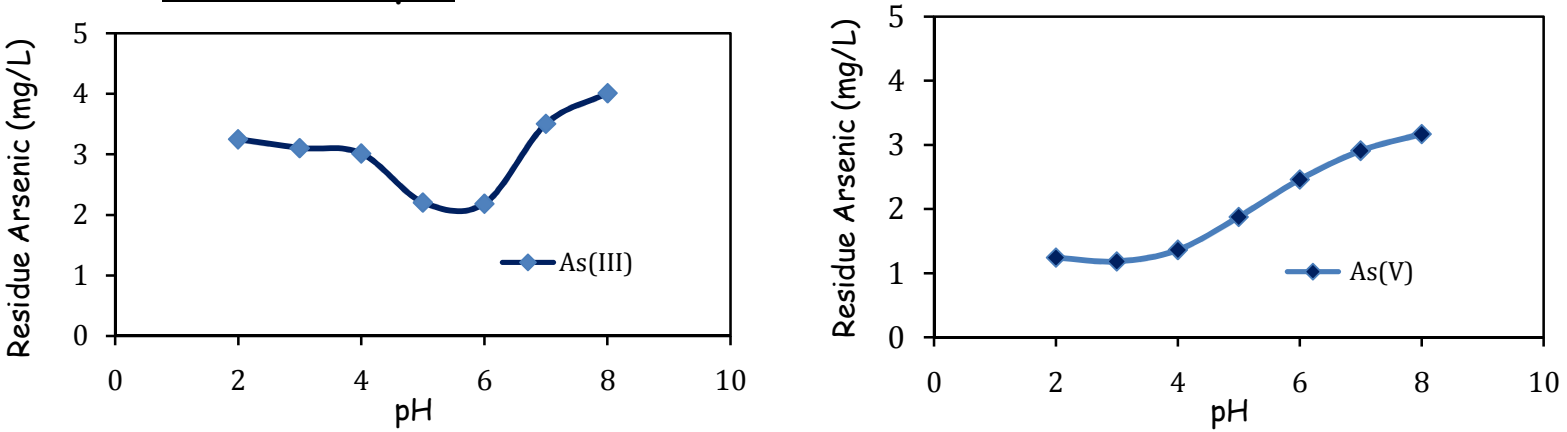
- pH
- Contact time
- Experiment temperature
- Adsorbent amount
- Initial arsenic concentration





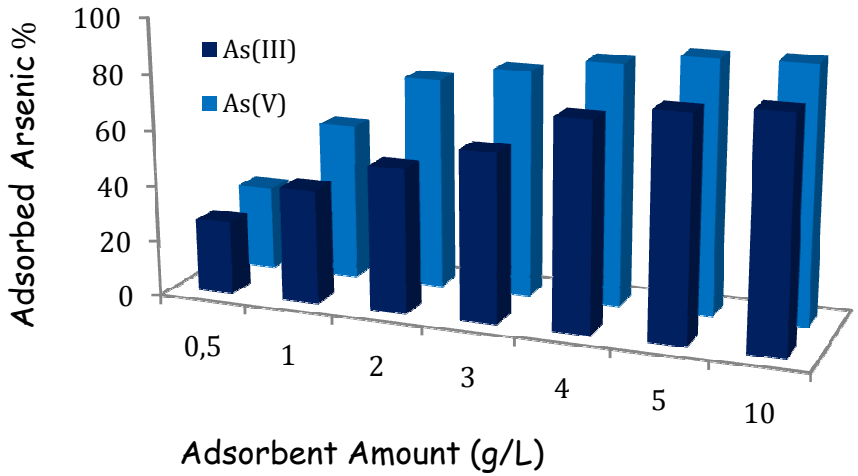
Experiment Results – Anatase

- Effect of pH

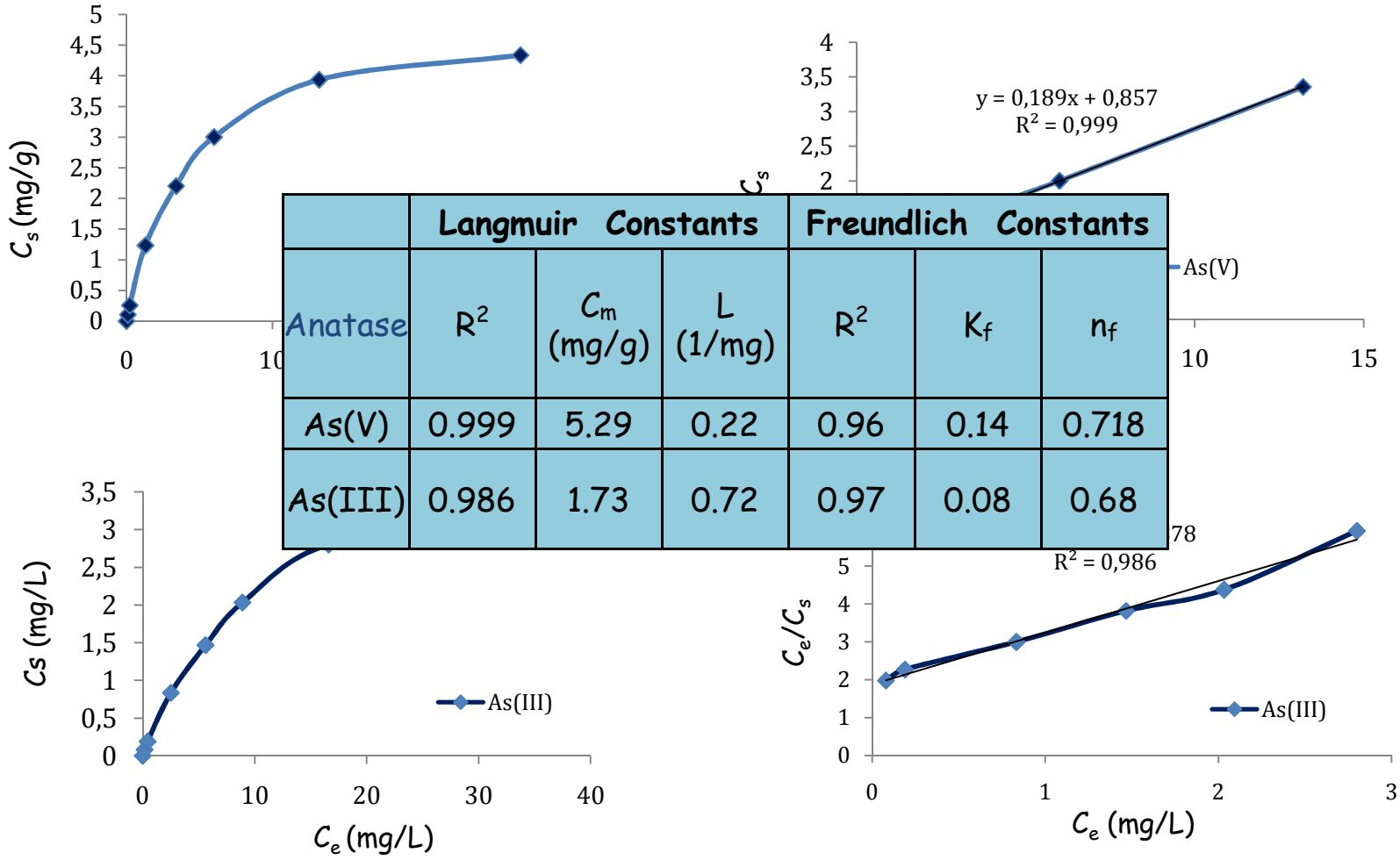


Initial arsenic concentration = 5 mg/L adsorbent amount = 3 g/L, contact time = 24 h

- Effect of Adsorbent Amount



Langmuir Isotherms – Anatase



	Langmuir Constants			Freundlich Constants		
Anatase	R^2	C_m (mg/g)	L (1/mg)	R^2	K_f	n_f
As(V)	0.999	5.29	0.22	0.96	0.14	0.718
As(III)	0.986	1.73	0.72	0.97	0.08	0.68

- 0.4, 1, 5, 10, 15, 25, 40 mg/l working solutions were prepared to obtain adsorption isotherms.

- Langmuir isotherm : $C_e / C_s = 1 / (C_m L) + C_e / C_m$
- Freundlich isotherm : $\ln C_s = \ln K_f + n_f \ln C_e$

Photocatalytic Oxidation of Arsenite

- Titania 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

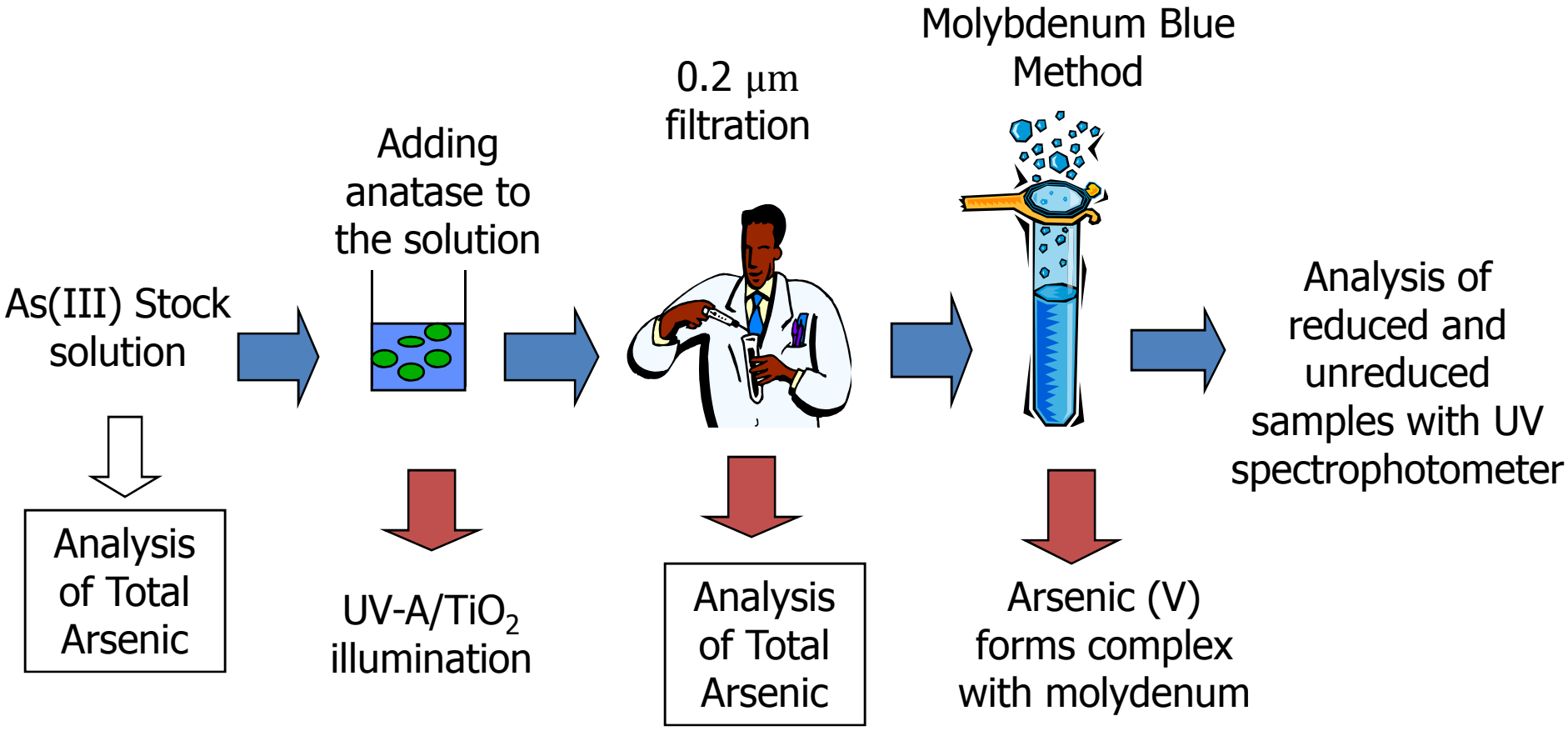
$$As(III) + HO^{\cdot} \rightarrow As(IV) + OH^- \quad (4)$$

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

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

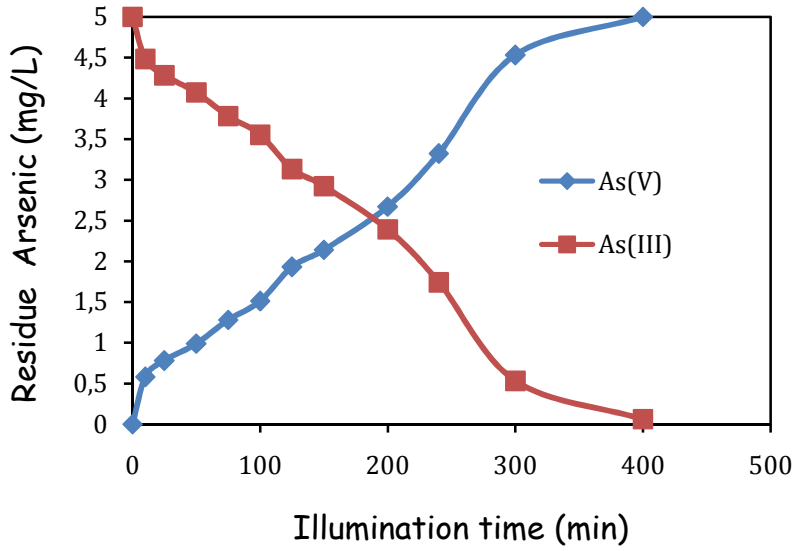
* Fu-Shen Zhang, Hideaki Itoh, (2006), Photocatalytic oxidation and removal of arsenite from water using slag-iron oxide-Tio2 adsorbent, Chemosphere 65, 125-131.

Photocatalytic Oxidation Experiment

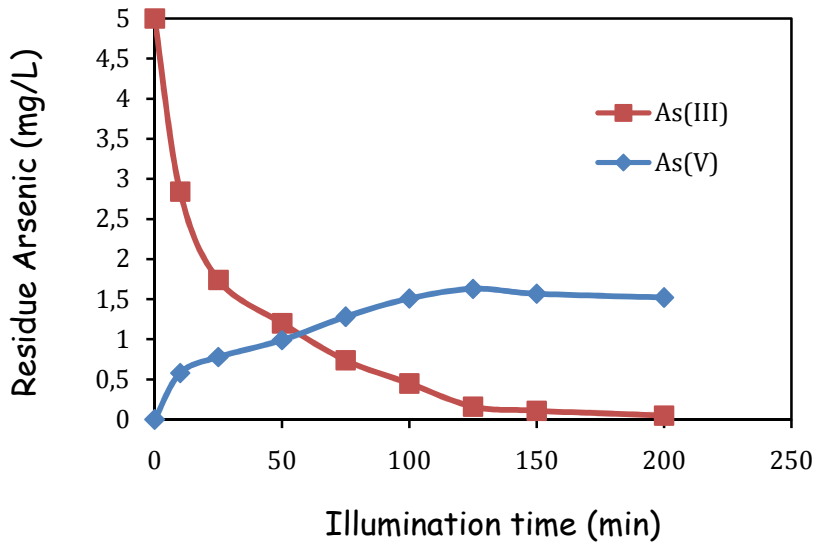


Effect of Illumination Time on Arsenic Removal

UV light only



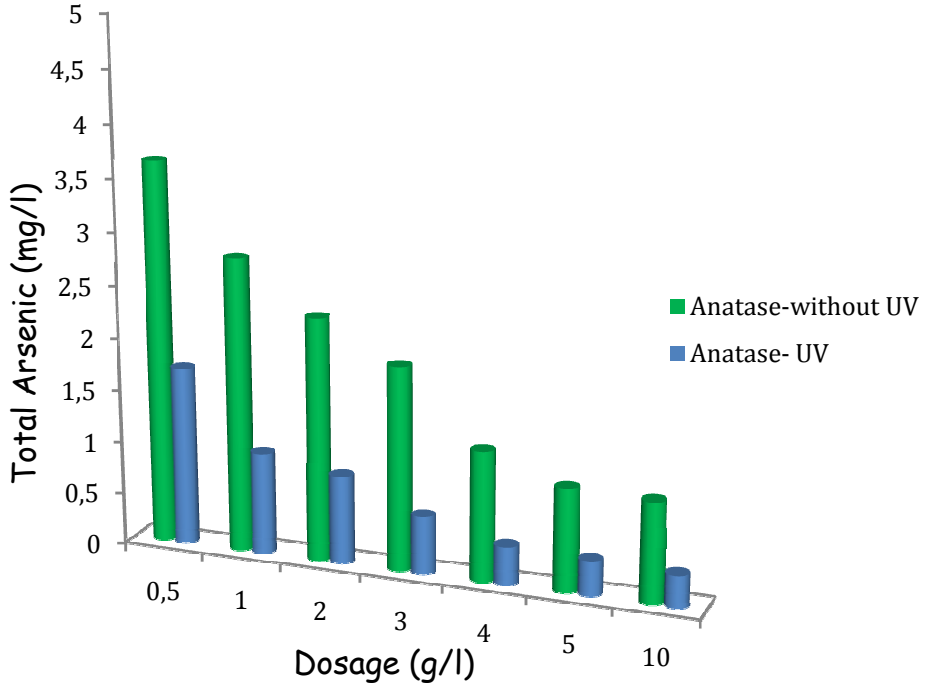
TiO_2 with UV light



- The effect of illumination time on arsenite oxidation was examined at an initial arsenite concentration of 5 mg /l and adsorbent amount 3 g/l at pH 3.

- 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.

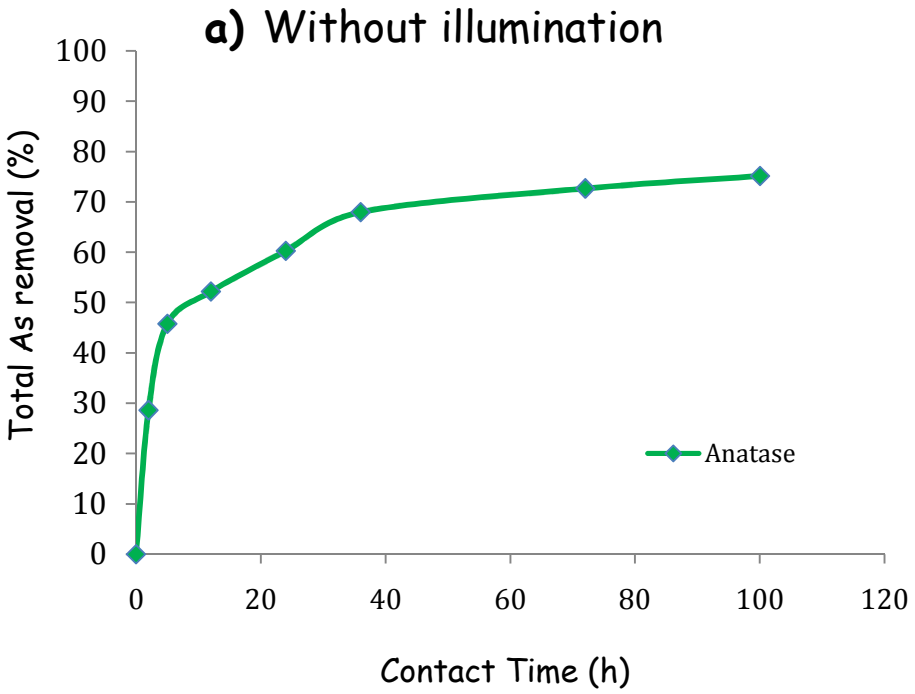
Effect of Adsorbent Amount on Total Arsenic Removal

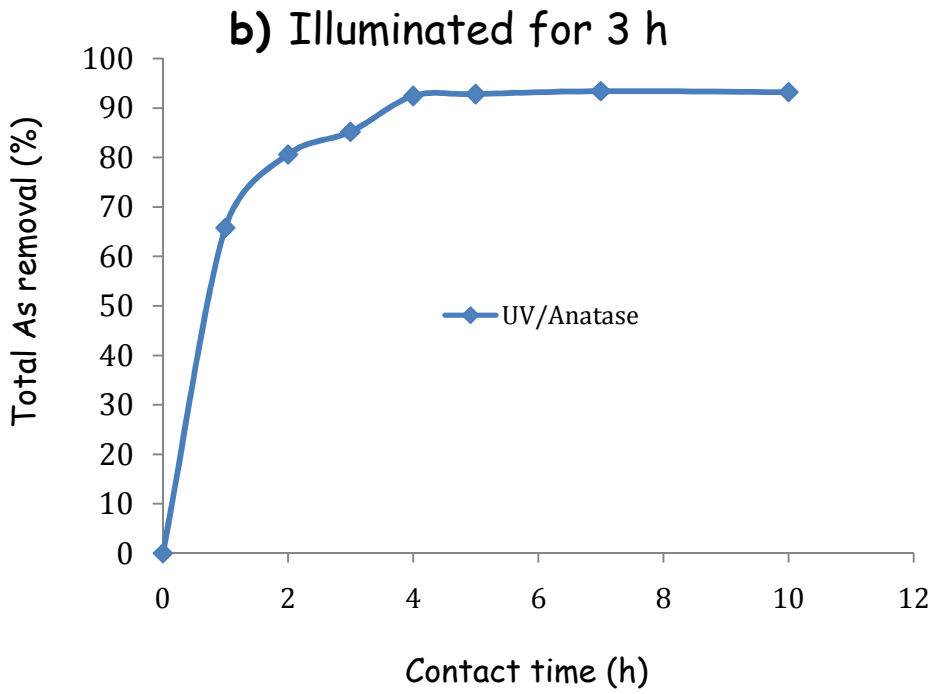


- Experimental conditions:
  - Illumination time = 3.5 h, contact time = 4 h.
  - Without illumination, contact time = 24 h.

- Arsenic removal efficieny is greatly affected by adsorbent dosage.
- The optimum application amount of the TiO_2 adsorbent is around 3-5 g/l for the photocatalytic experiment .

Effect of Contact time





- Experimental conditions:
  - Anatase dosage = 3 g/L, pH = 3, 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.

Conclusion

- By using sol-gel method, anatase crystal was synthesized with particle size between 40-100 nm.
- Adsorption experiments were performed for anatase to obtain optimum pH, contact time and adsorbent amount.
- The low adsorption capacity of anatase 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 total arsenic from water was improved by UV- irradiation about 50% as compared with adsorption process of anatase.

Thank you!