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6th Sustainable Nanotechnology Conference,2017

Arsenic Removal by Graphene Oxide-Nanoscale Zero-valent Iron Hybrid

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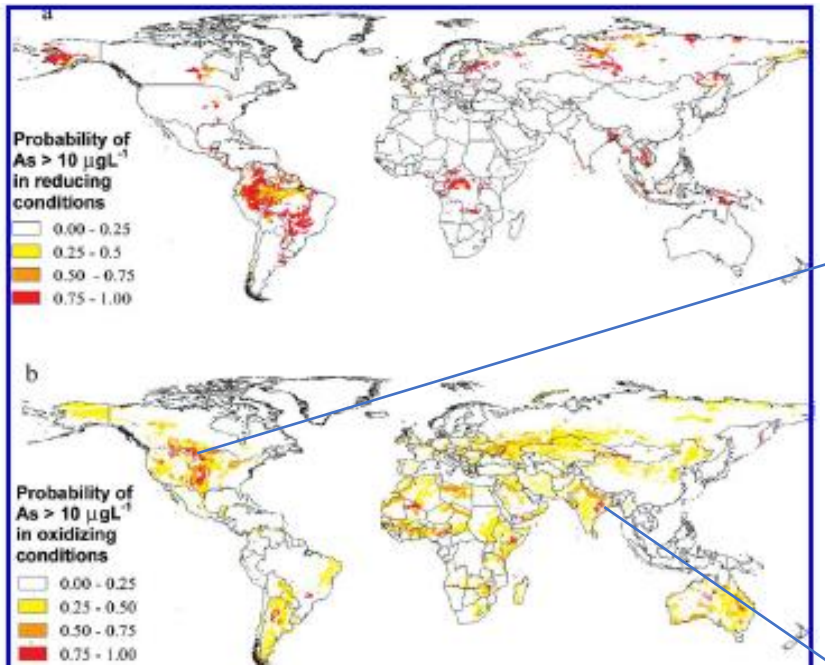
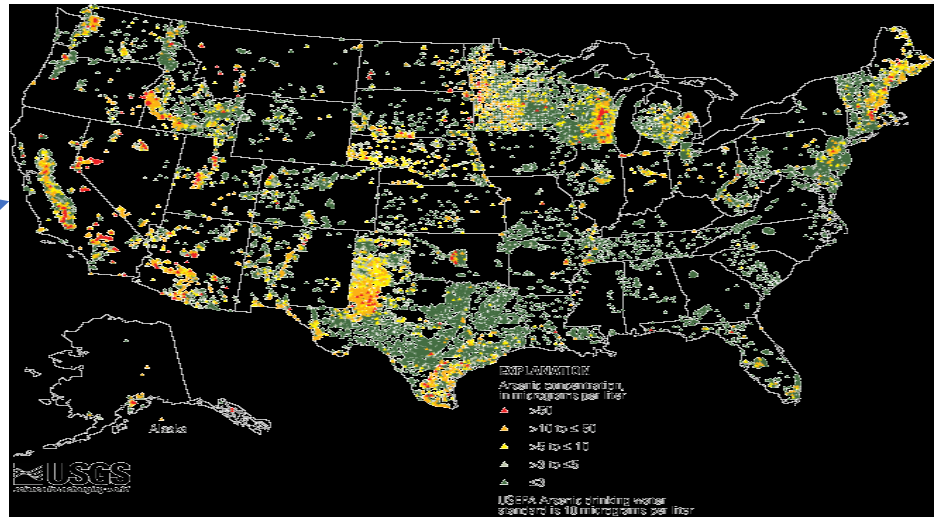
Outline

- Arsenic contamination
- Concept of graphene oxide based material
- Material synthesis and characterization
- Arsenic Removal and Mechanisms
- Desorption Study
- Conclusion

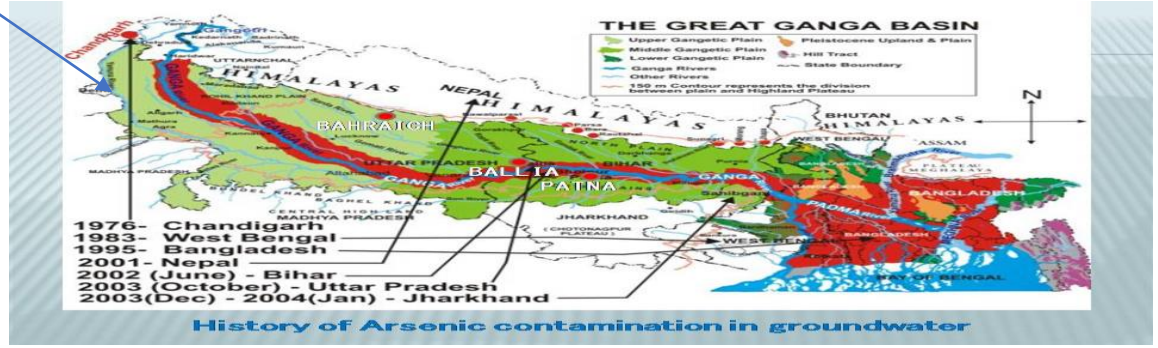
Global Contamination



Global Status Amini et al. 2008

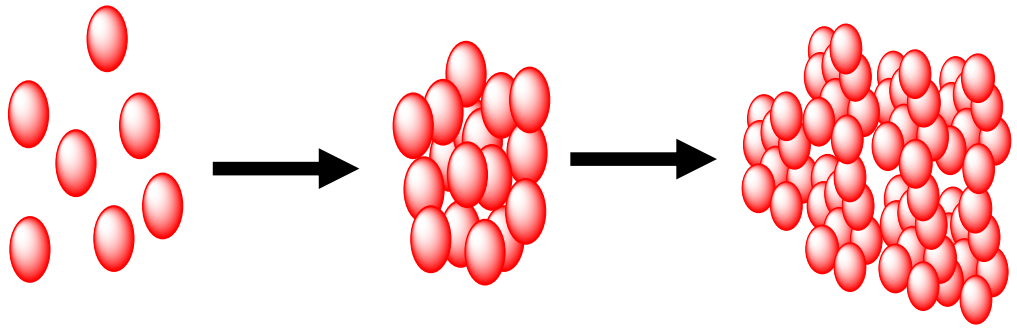


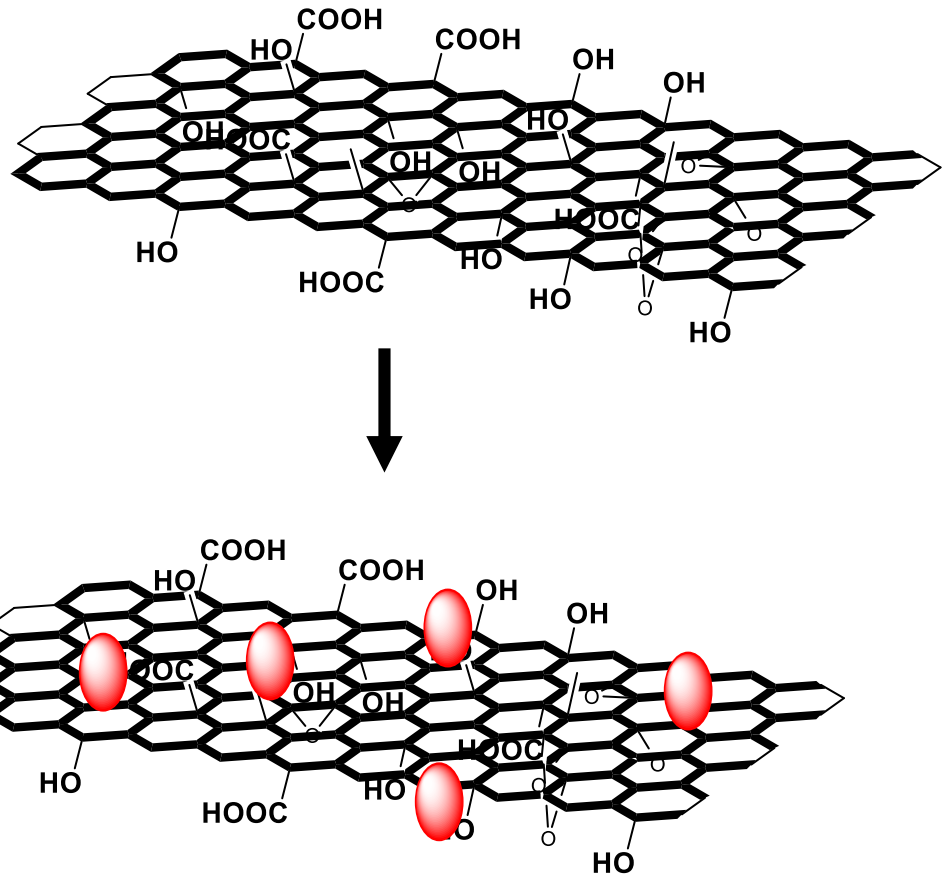
USA Status (USGS, 2014)



India and Bangladesh

Concept of Graphene Oxide Based Composites





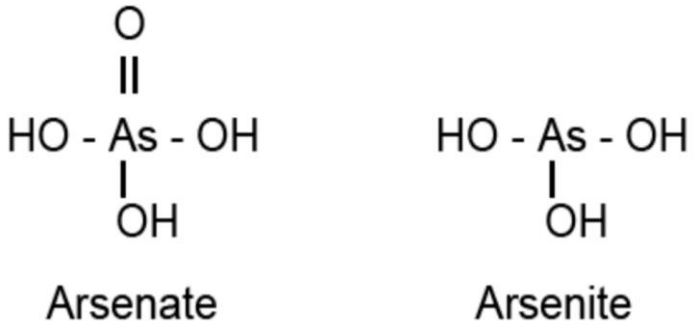
- Platform to build new adsorbents
- Two basal planes available
- High dispersion

Research Background

- Arsenic (As) is toxic, carcinogenic, non-biodegradable, and persistence metalloid
- MCL in drinking water 10 µg/L (WHO)
- Adsorbent with high adsorption capacity and selectivity
- Iron nanoparticles (Fe NPs) show high selectivity to As
- Fe NPs is highly agglomerate
- Graphene oxide is single layer structure of carbon having high stability and negatively charged surface

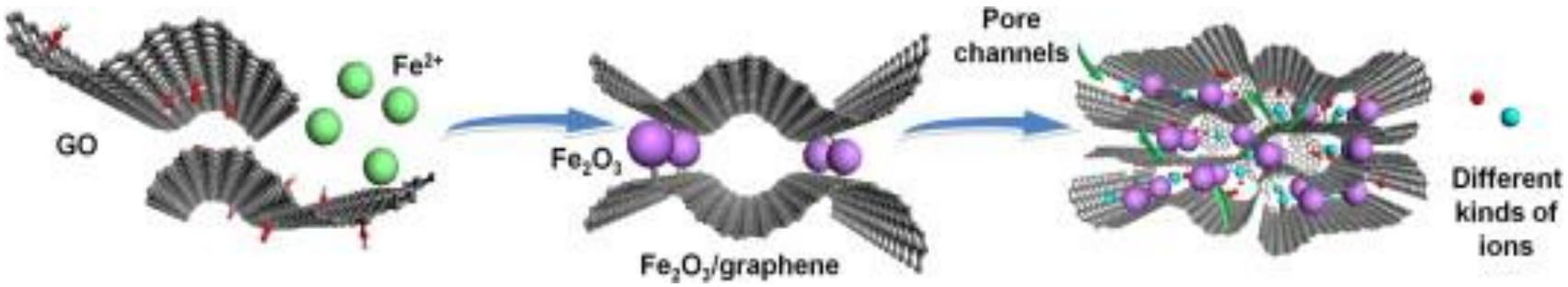
Objectives

- Evaluation of graphene-supported Fe NPs and conventional Fe NPs for arsenic removal and their possible mechanisms.
- Effectiveness under different environmental conditions
- Desorption pattern

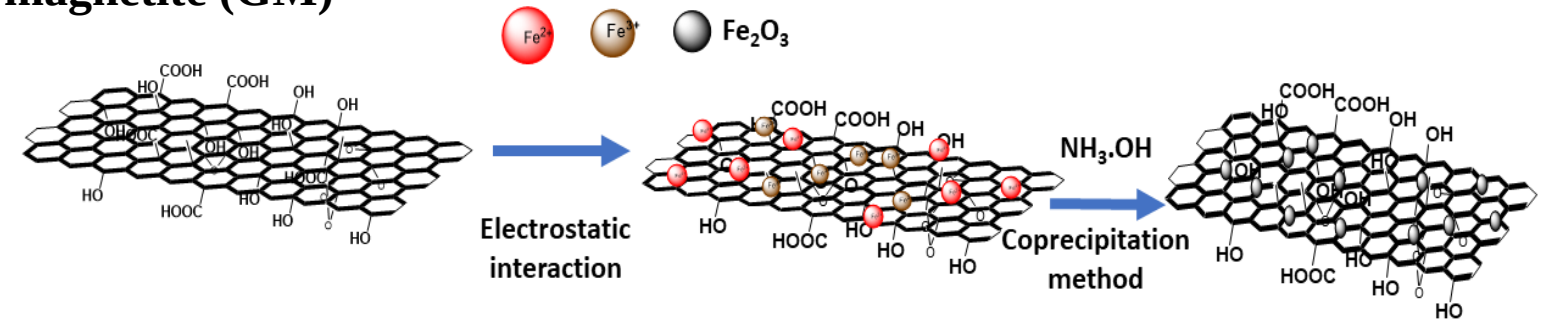


Arsenate Arsenite

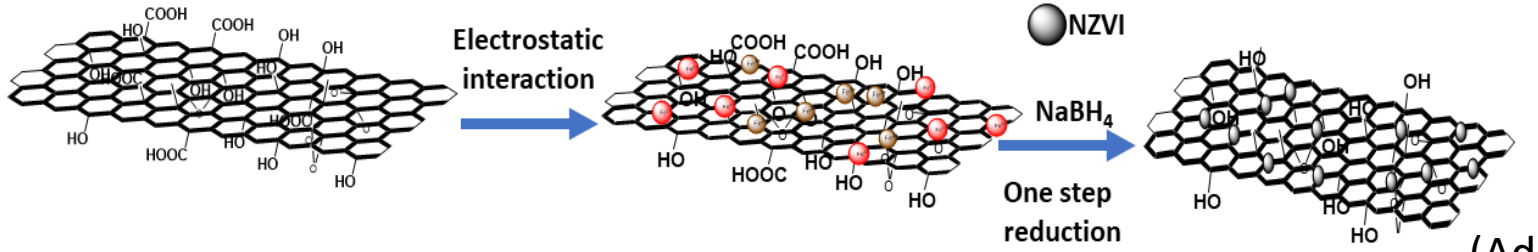
Synthesis Pathway of Graphene-Fe Hybrid



Graphene oxide magnetite (GM)



Graphene oxide nanoscale zerovalent iron (GNZVI)



(Adopted from Li *et al.*, 2014)

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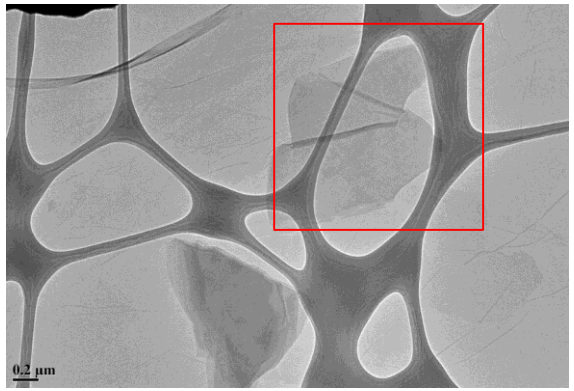
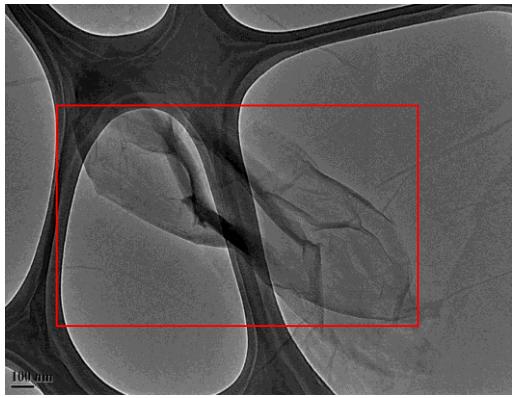
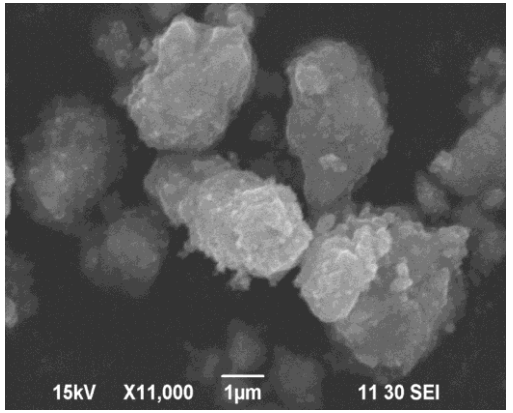
Material Characterization

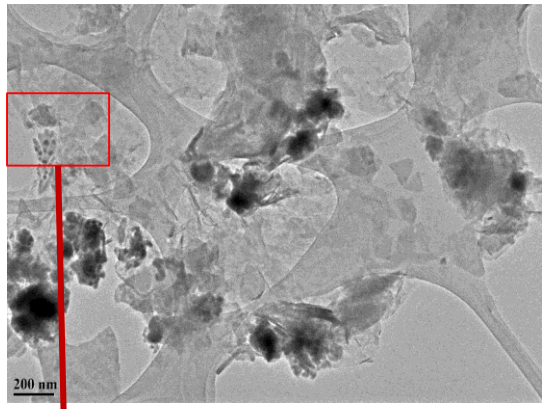
Graphene Oxide

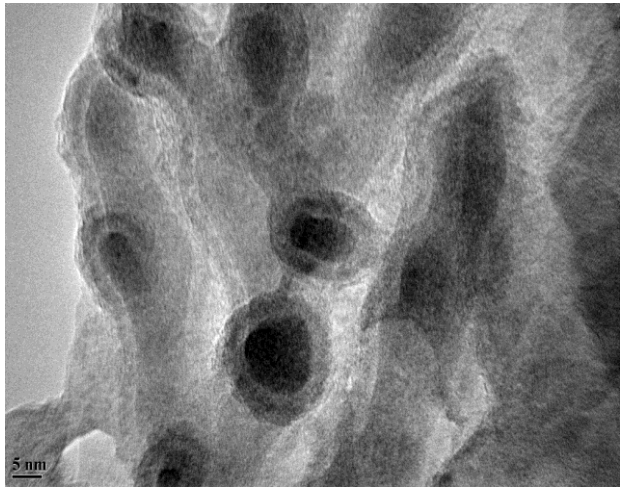




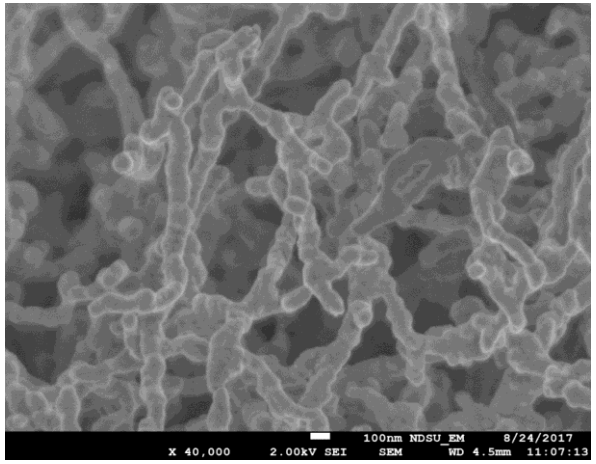
GNZVI

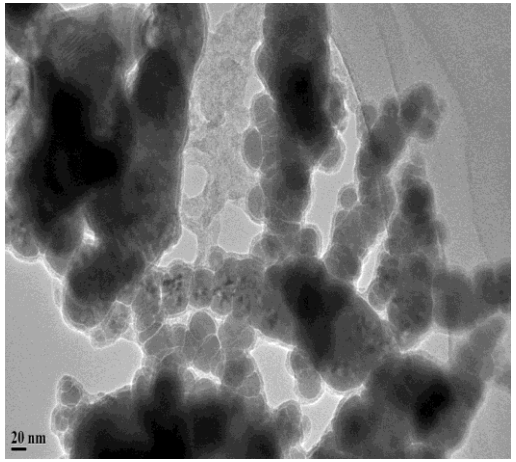






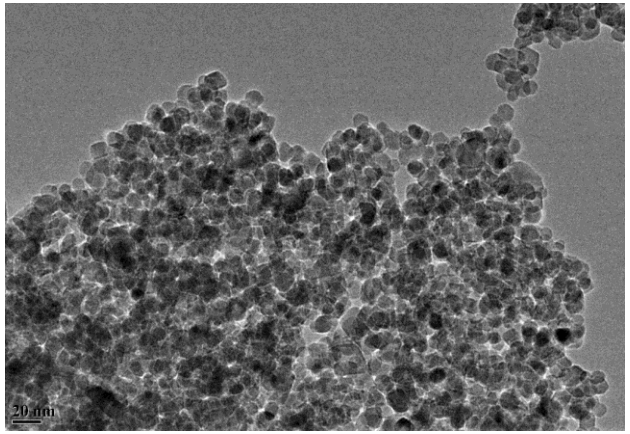
NZVI



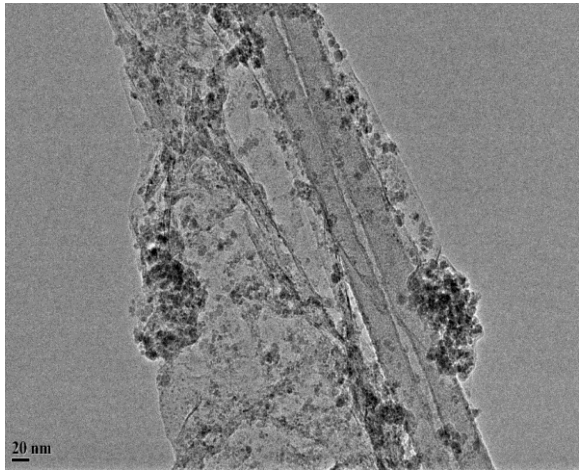


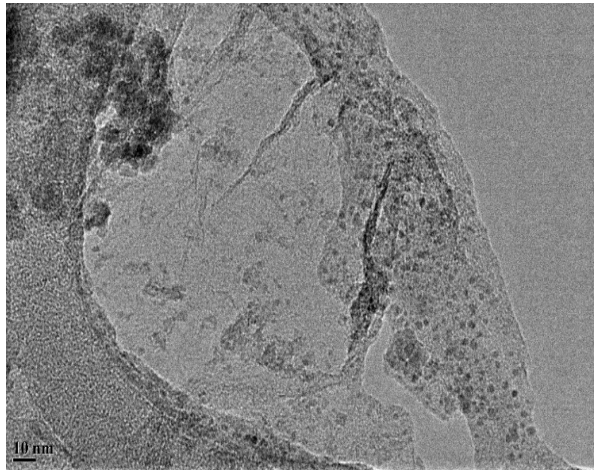
Material Characterization

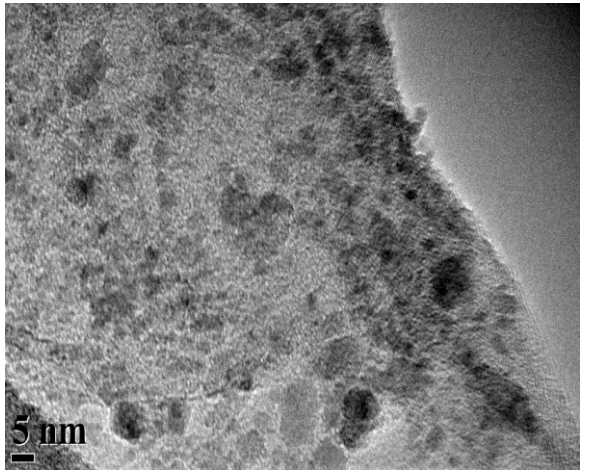
Magnetite



GM

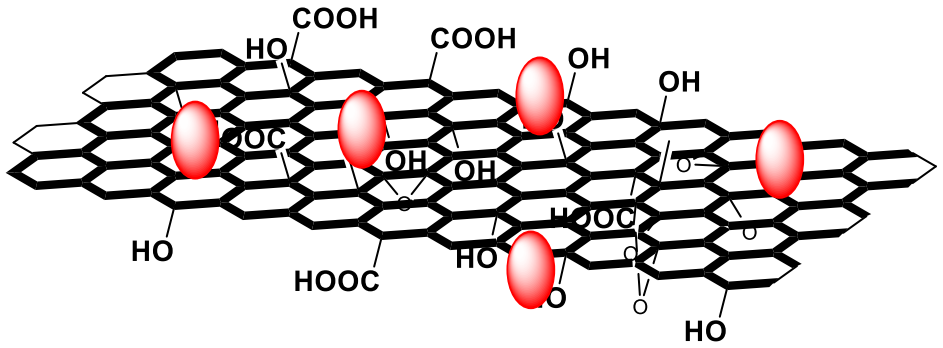




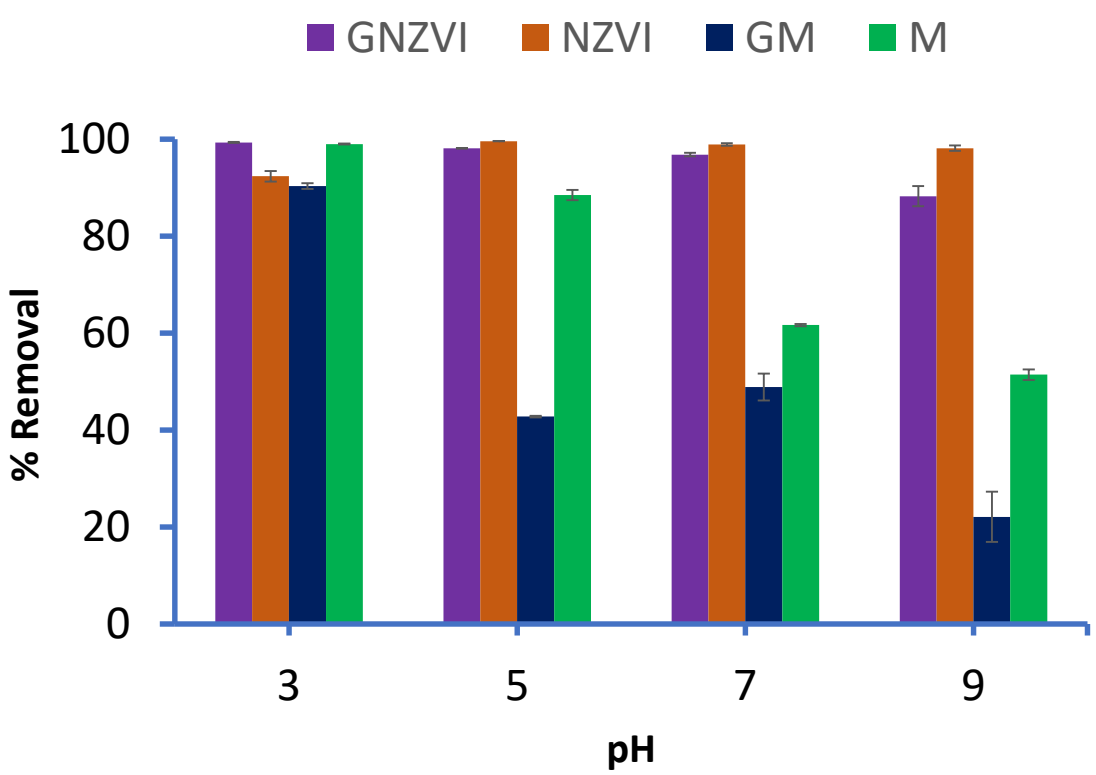


Advantages of Graphene-Oxide Supported Fe-Nps

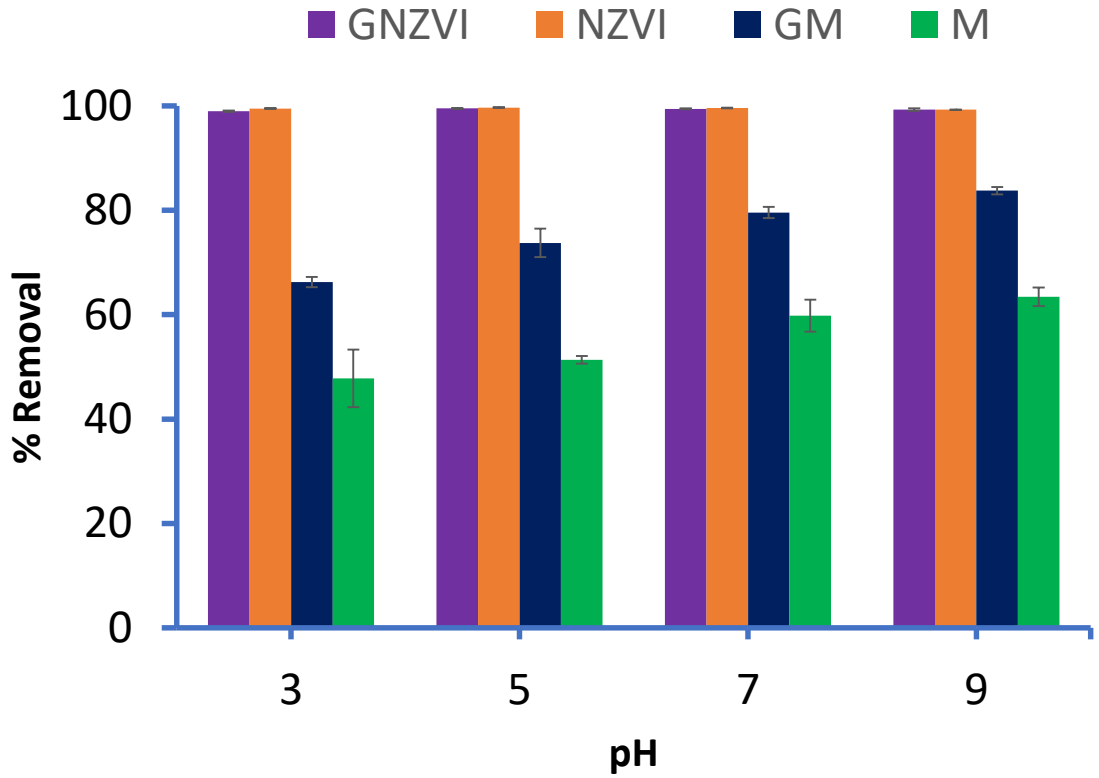
- Less agglomeration
- Better exposure to Arsenic Solution
- Higher Removal



As Removal by Batch Study



As(V)



As(III)

C_0= 5 mg/L
Adsorbent: 250 mg/L

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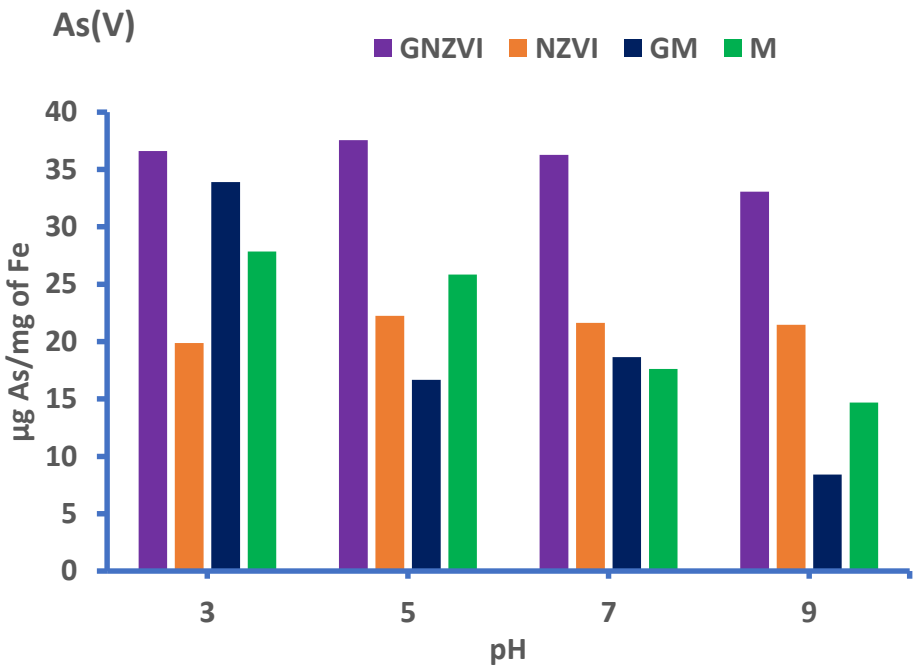
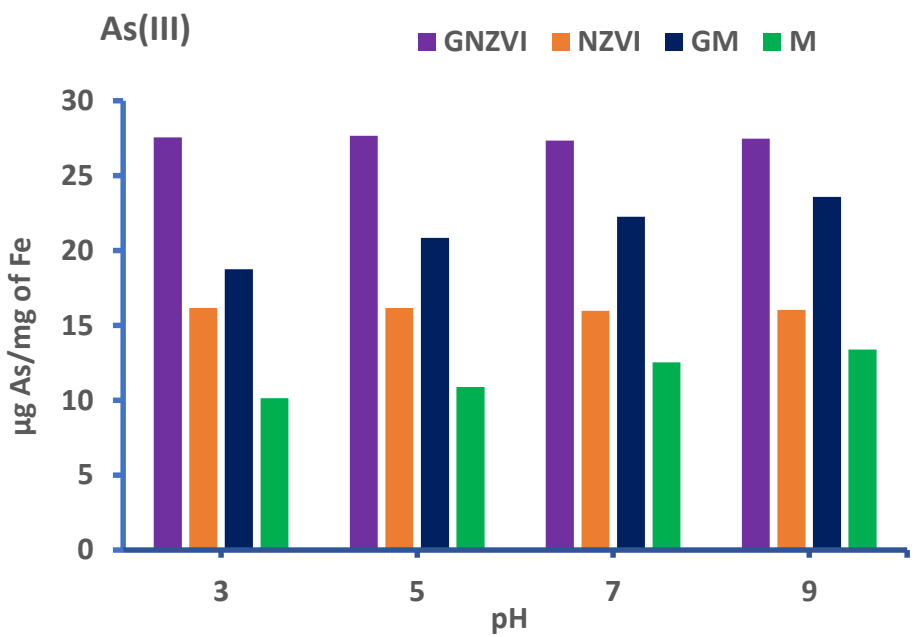
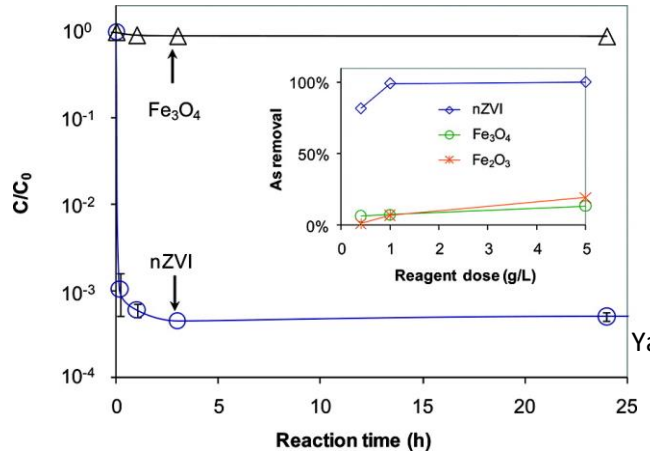
Arsenic Removal on Fe Content Basis





In 10mg	mg Fe
• GNZVI	5.545
• NZVI	9.5
• GM	5.45
• M	7.27



Yan et al., 2012

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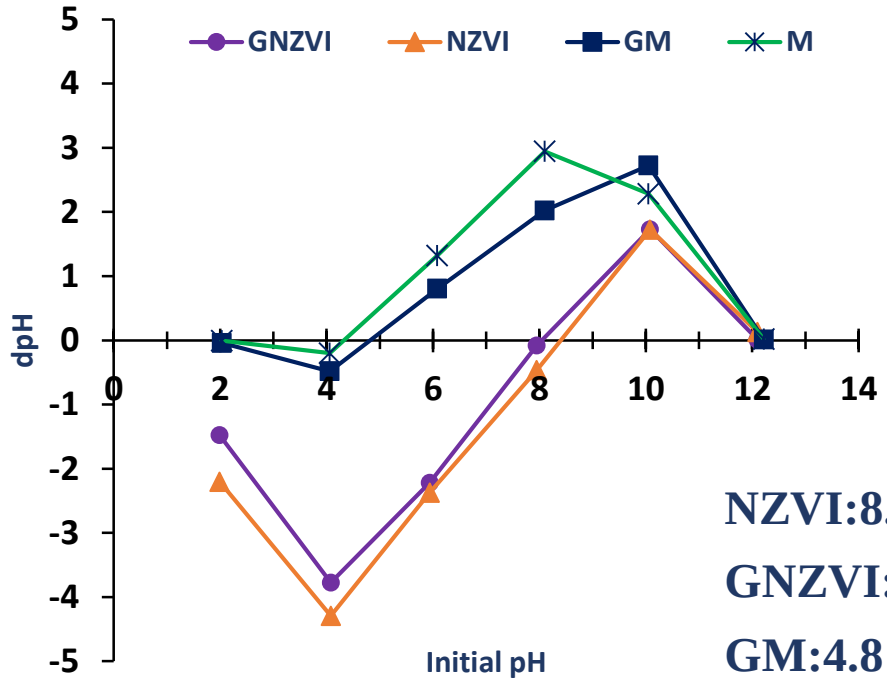
Zeta Potential (mV) and Point of Zero Charge

Adsorbent	Mean	pH
GO	-48.50±0.33	8.70
GNZVI	-22.97±0.90	8.58
GNZVI+As	-38.13±0.98	8.79
NZVI	11.67±0.87	8.9
NZVI+As	7.26±0.47	8.85
GM	-10.76±0.87	7.78
GM+As	-26.70±0.24	4.77
M	8.27±1.19	8.01
M+As	-14.07±0.71	4.38



NZVI:8.4

GNZVI:8.05

GM:4.8

M:4.3

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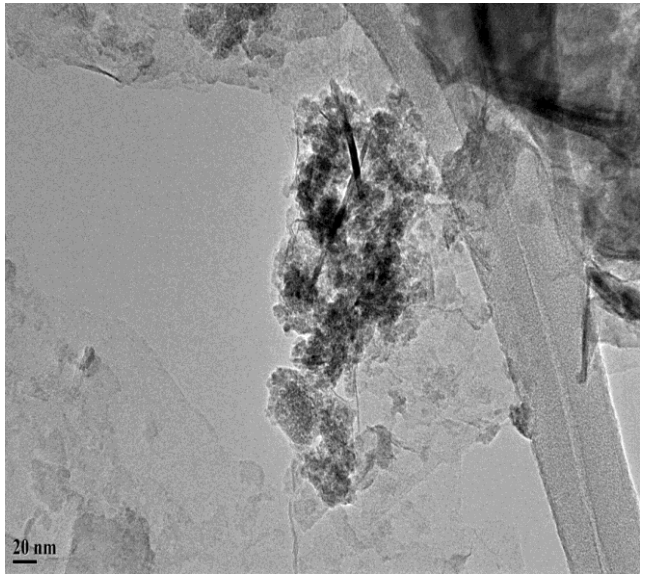
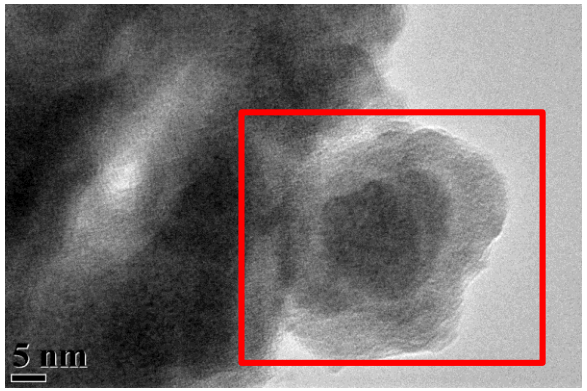
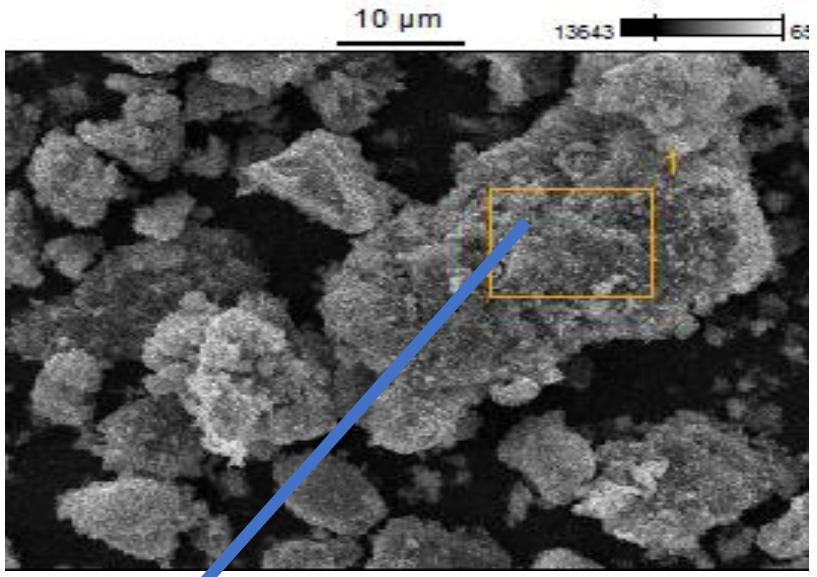
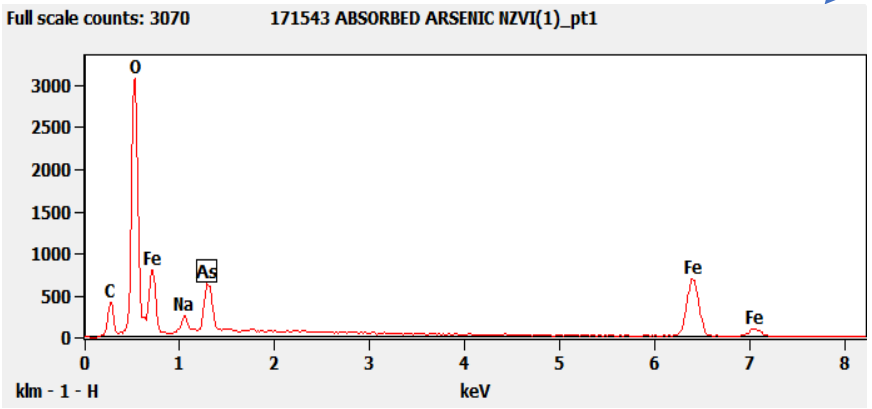
Adsorbed Arsenic in GNZVI









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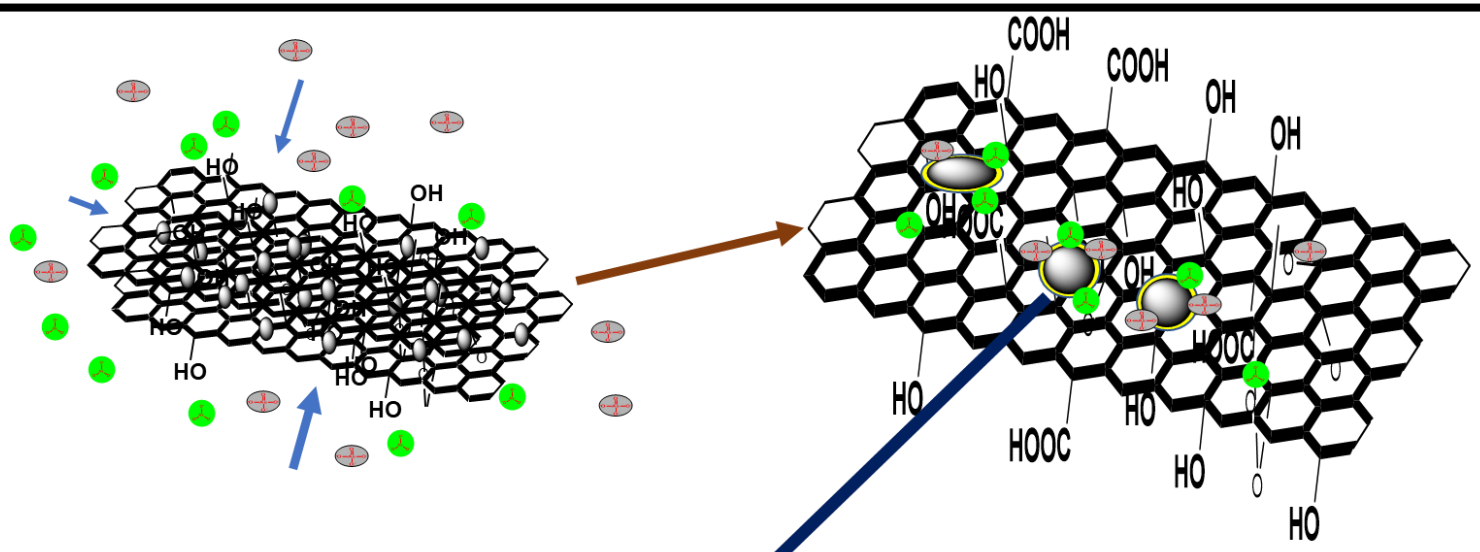
Mechanisms for GNZVI


COOH
COOH
OH
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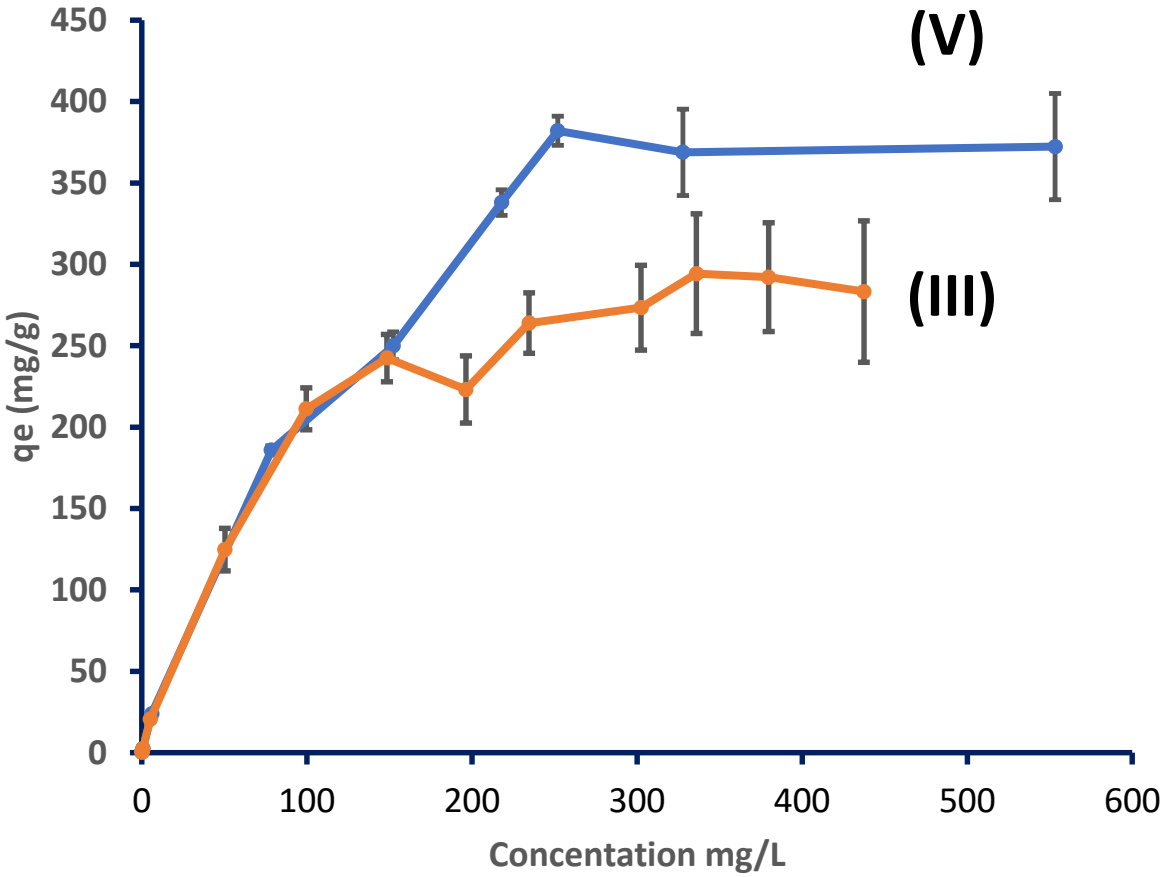
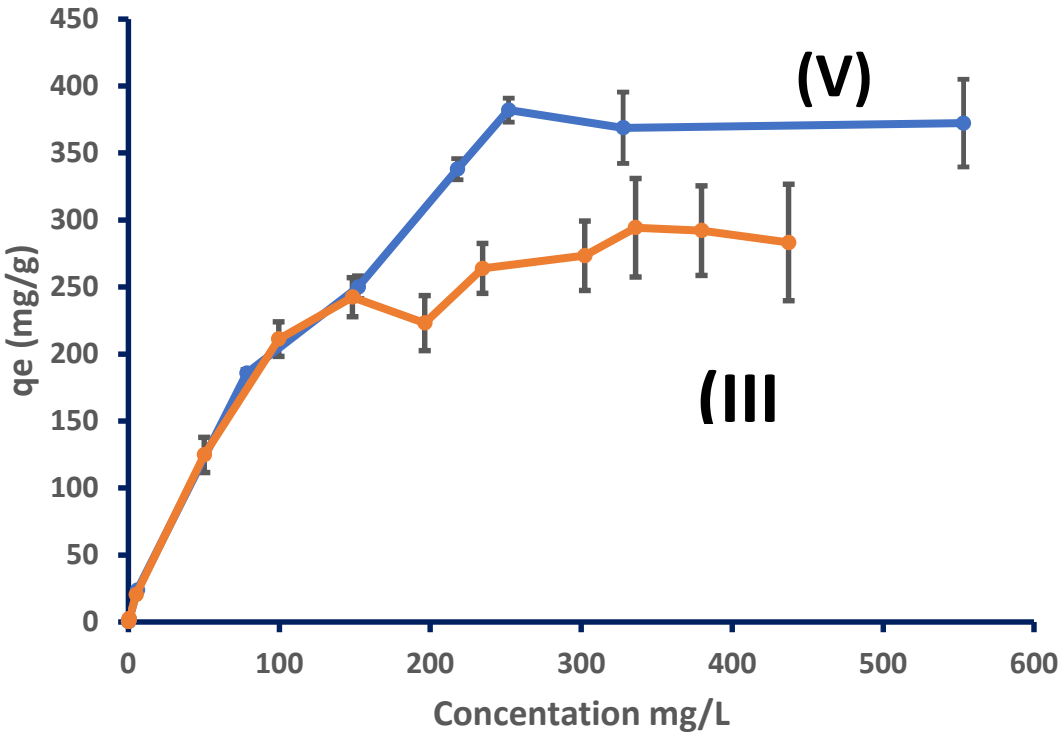
HO

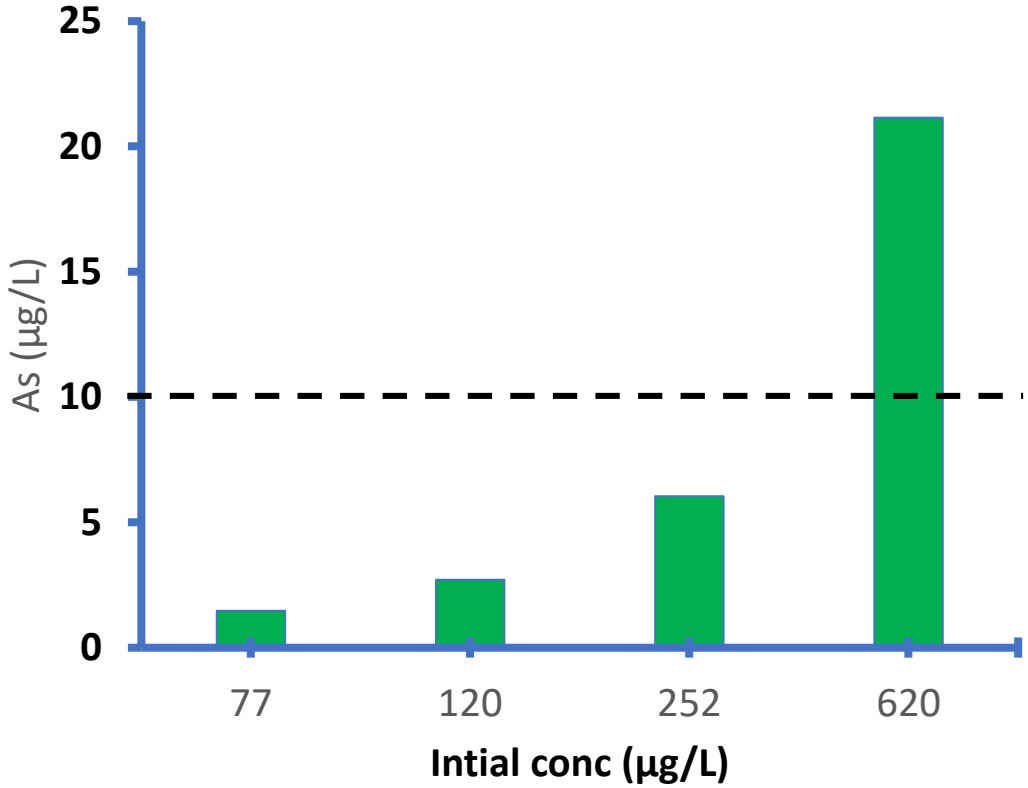
Adsorption Isotherm of GNZVI



	Langmuir		Freundlich	
As(V)	q_m (mg/g)	384.62	n	1.779
	K_l(L/mg)	0.092	k_f	20.649
	R^2	0.9814	R^2	0.9617
As(III)	q_m (mg/g)	294.12	n	2.15
	K_l(L/mg)	0.084	k_f	24.31
	R^2	0.99	R^2	0.8672

Low Concentration Removal





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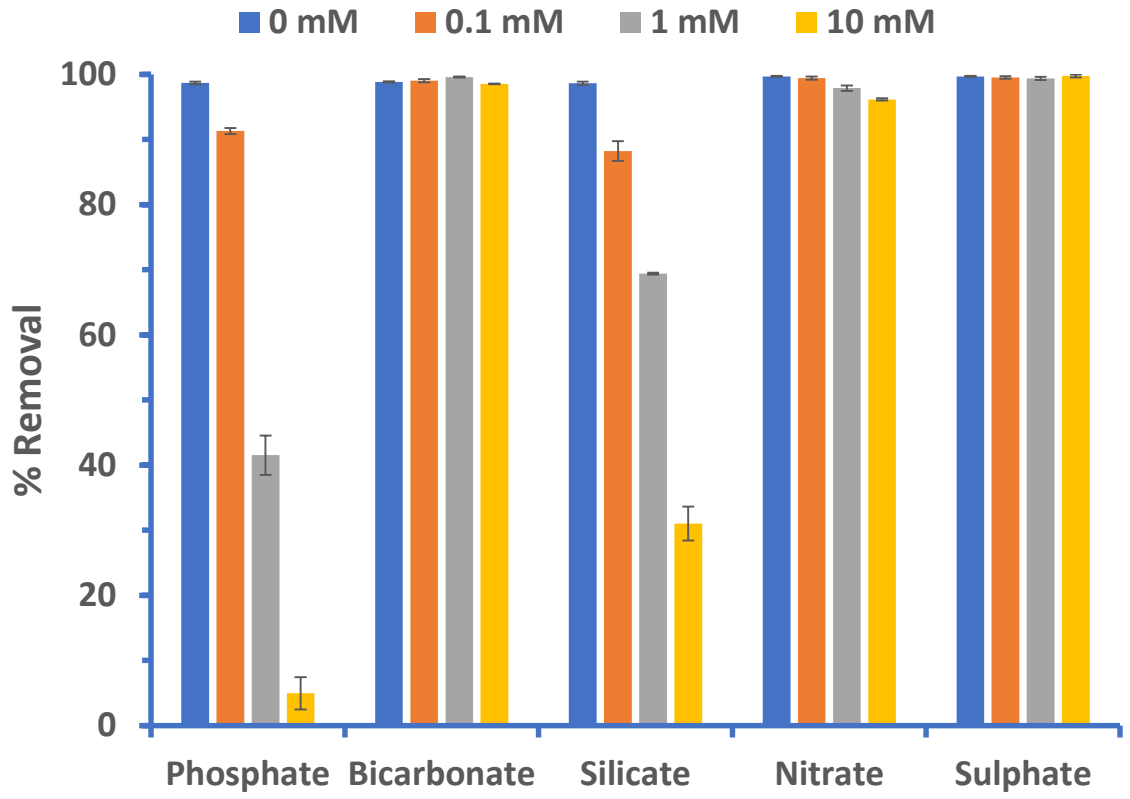
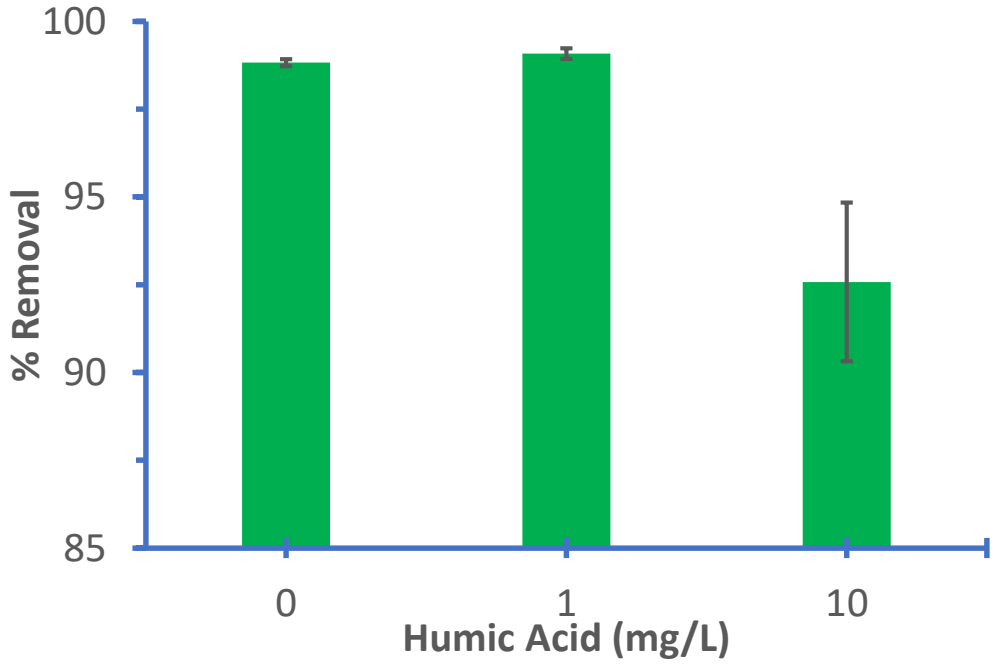
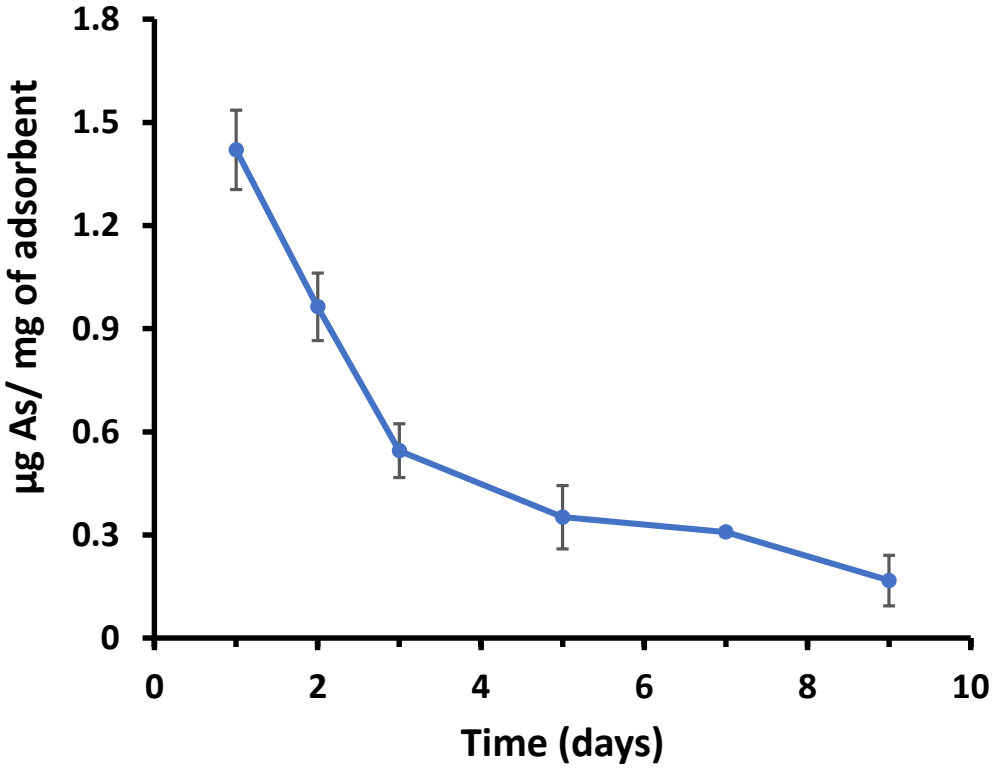
Interferences on As(V) removal by GNZVI



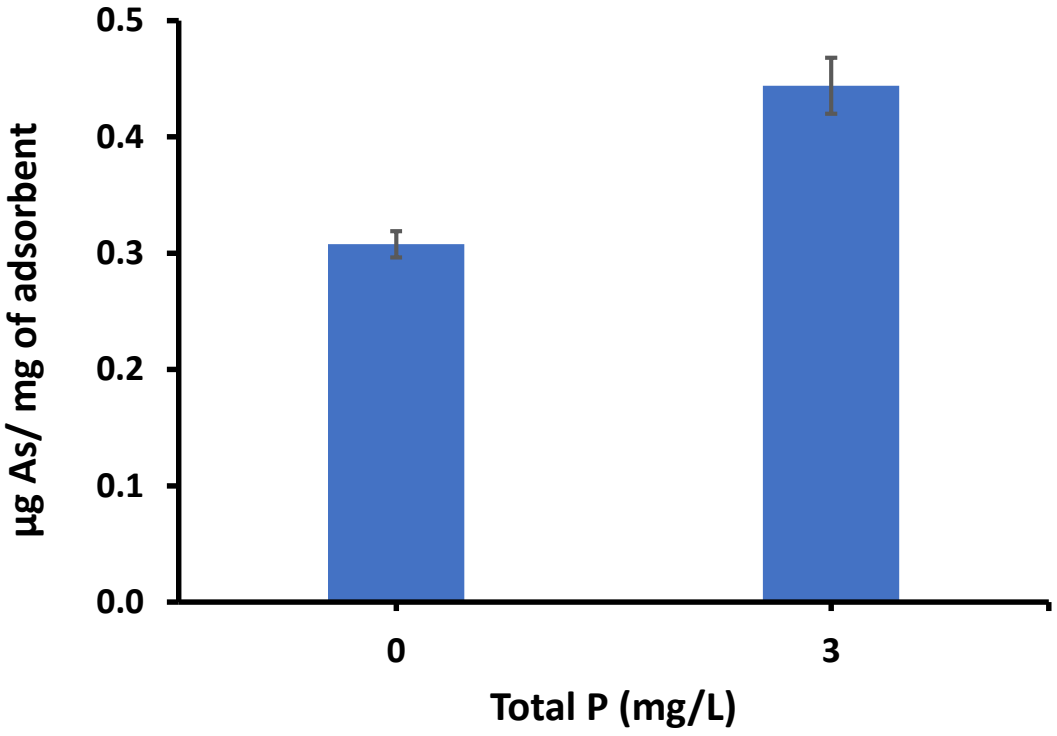


Desorption of Arsenic from Nano-Composite

Release in DI Water



Release in Synthetic Groundwater



Adsorbed As: 110 µg /mg of GNZVI

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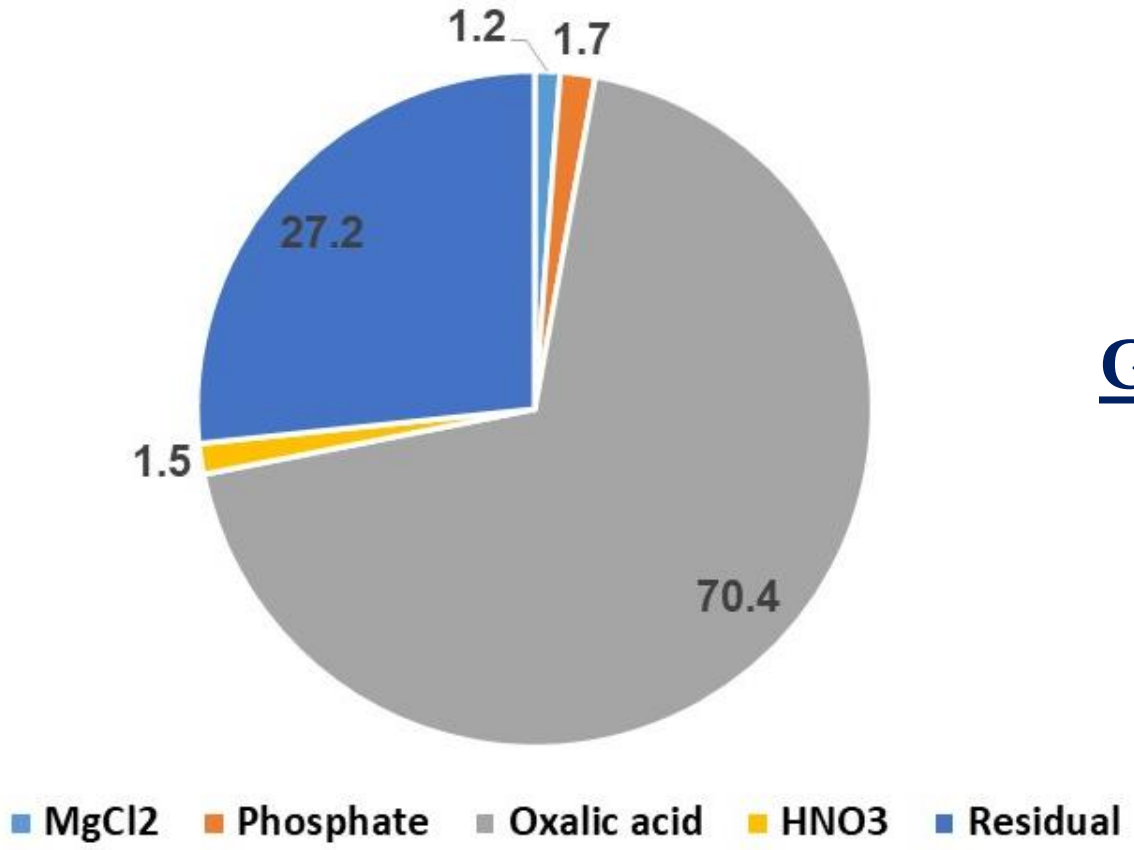
Sequential Extraction

Extractant	Target phase
$Mgcl_2$	ionically bound As
Phosphate	strongly adsorbed As
Oxalic acid	As coprecipitated with amorphous Fe oxyhydroxides
HNO_3	As coprecipitated with crystalline Fe oxyhydroxides

Keon, 2001



GNZVI

Conclusions

- Graphene oxide iron nanocomposites having better removal
- The GNZVI recorded high adsorption capacity
- Works effectively under variable environmental condition
- Low As desorption from adsorbed phase

Acknowledgments

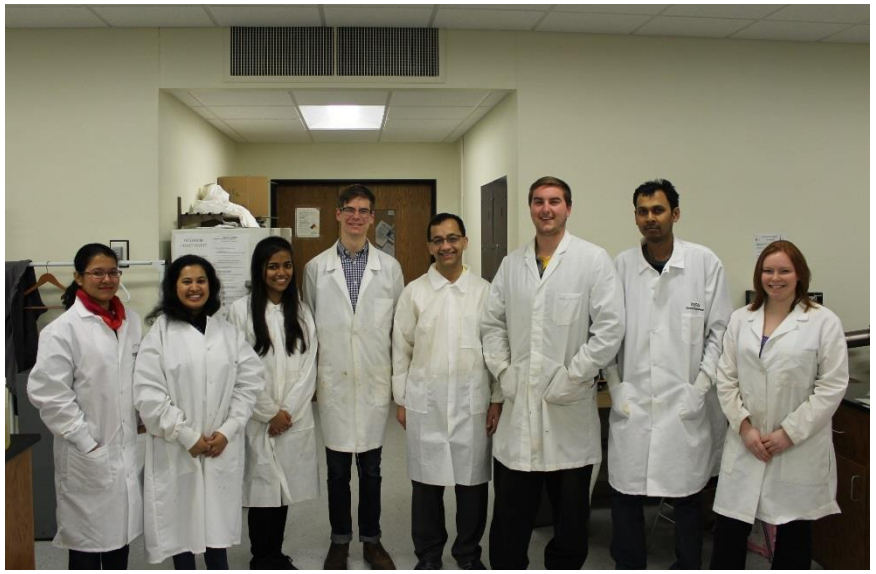
National Science Foundation (CBET-1707093)

Indian Council of Agricultural Research, Govt of India

NDSU Office of Research and Creative Activity (Grand Challenge Award)

Dr. Sudipta Seal , Materials Science and Engineering, UCF

Member of Nanoenvirology Research Group



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Comments and suggestion

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Thank You ...

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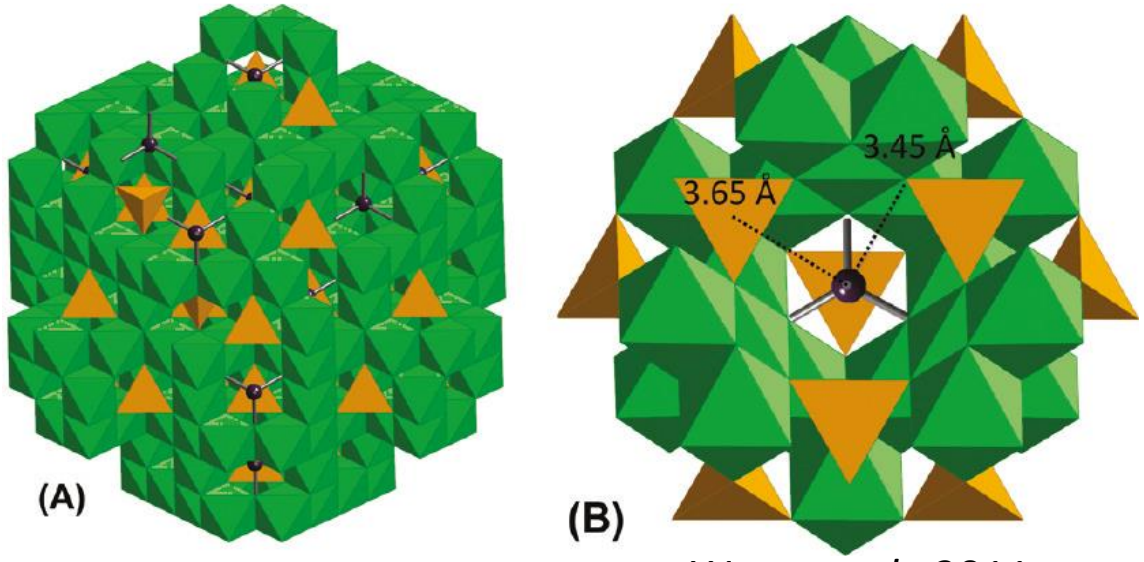
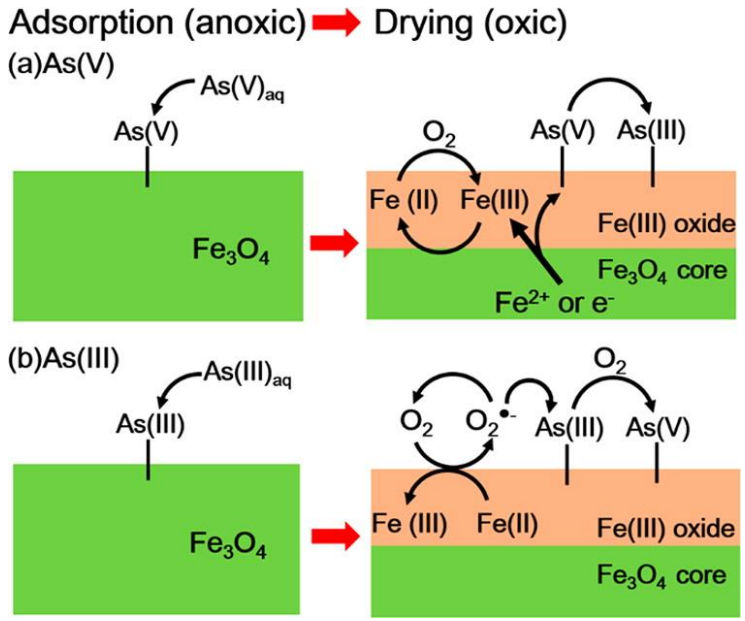
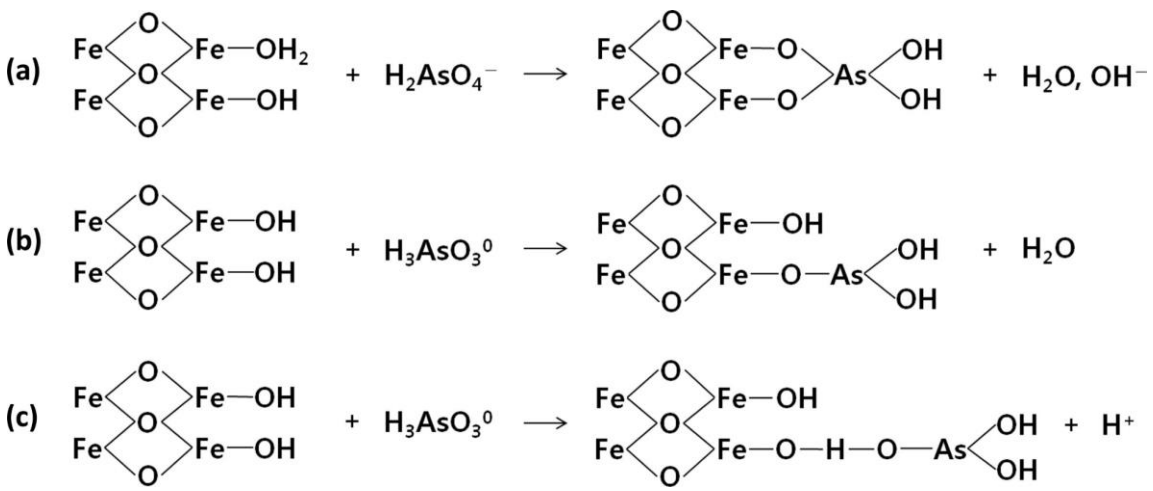


Wang *et al.,* 2011

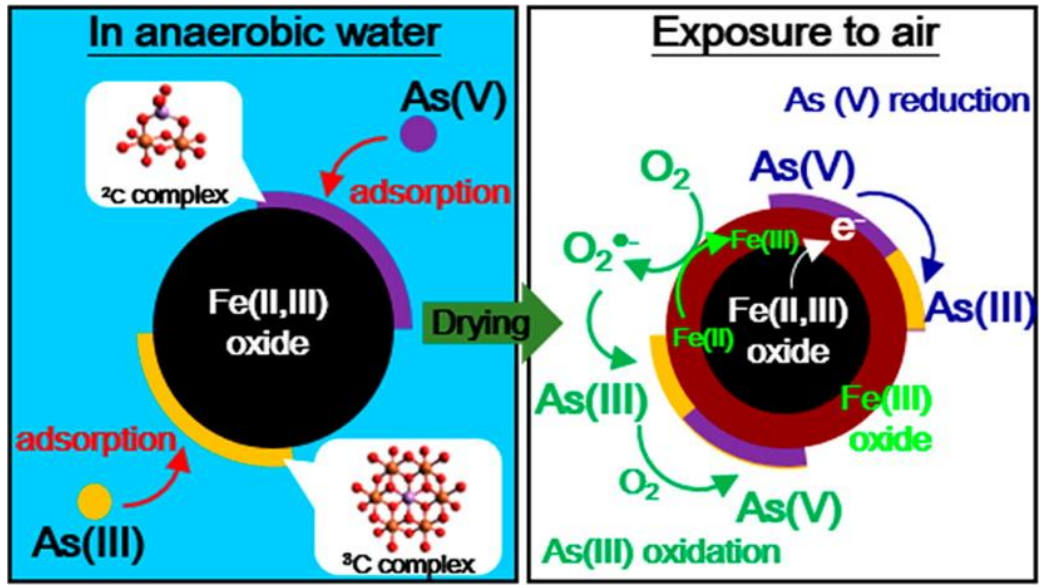


Liu *et al.,* 2015

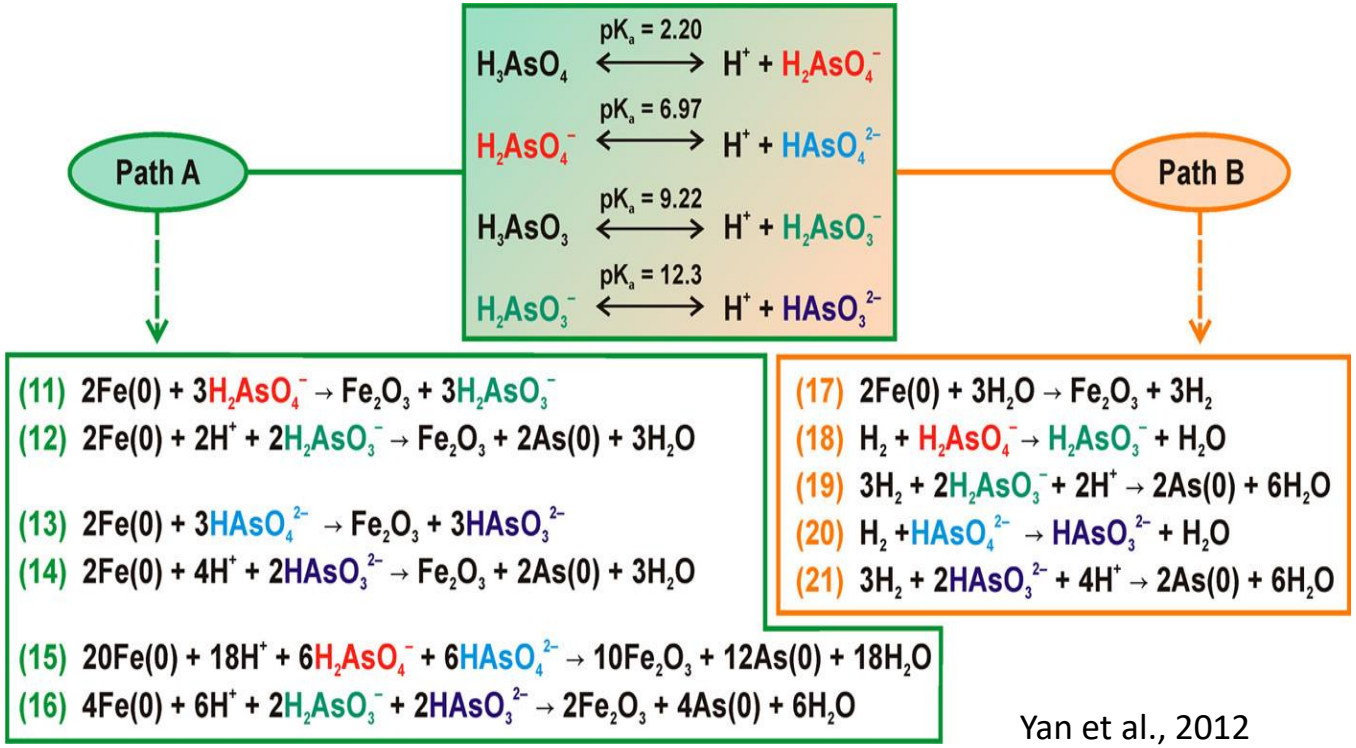


(a) bidentate binuclear–bridging complex for As(V), (b) monodentate complex for As(III), (c) outer-sphere complex for As(III).

Yahoon *et al.,* 2016

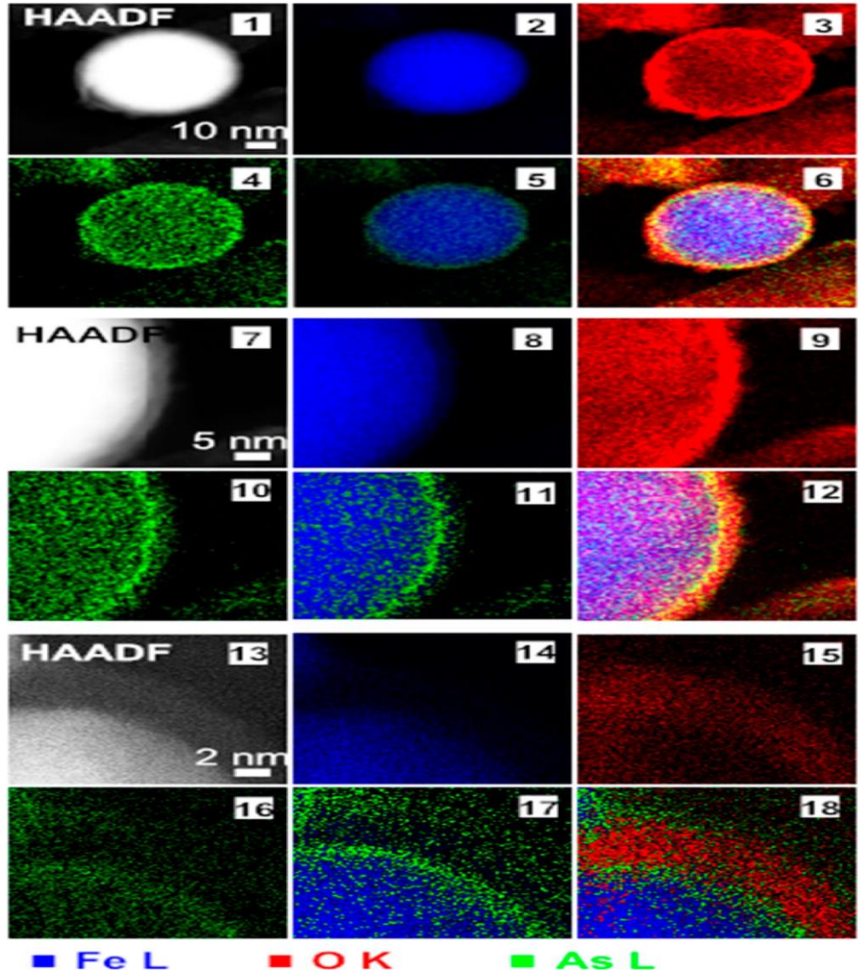


Liu *et al.,* 2015



Yan et al., 2012

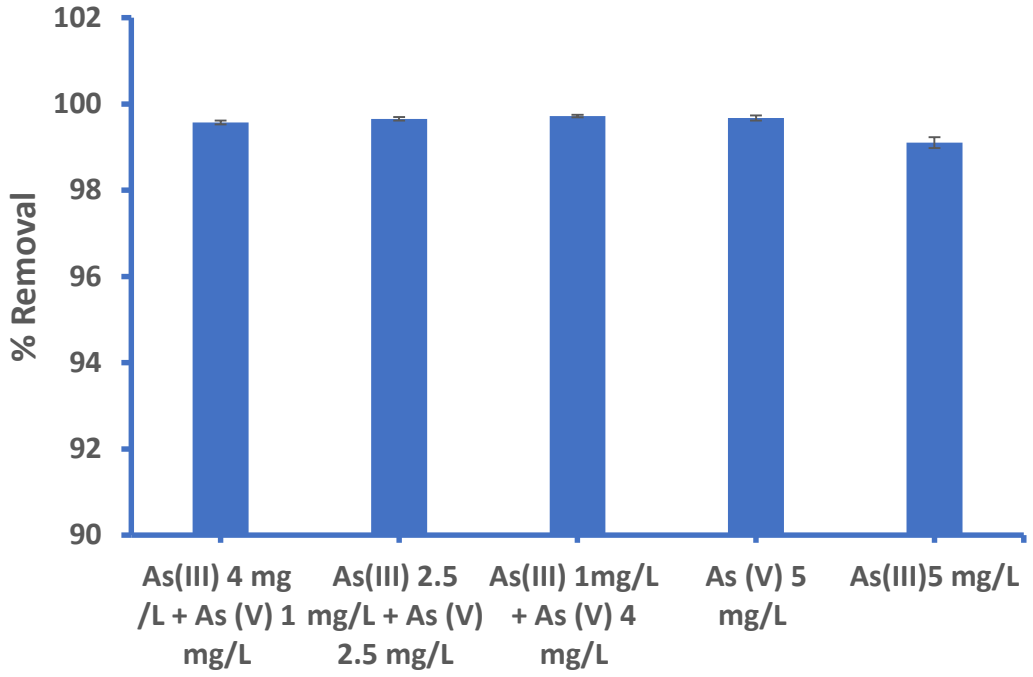
Reduction potential of NZVI & As(V)-to-As(0) −0.447 V (Fe/Fe(II)), and . 0.499 V



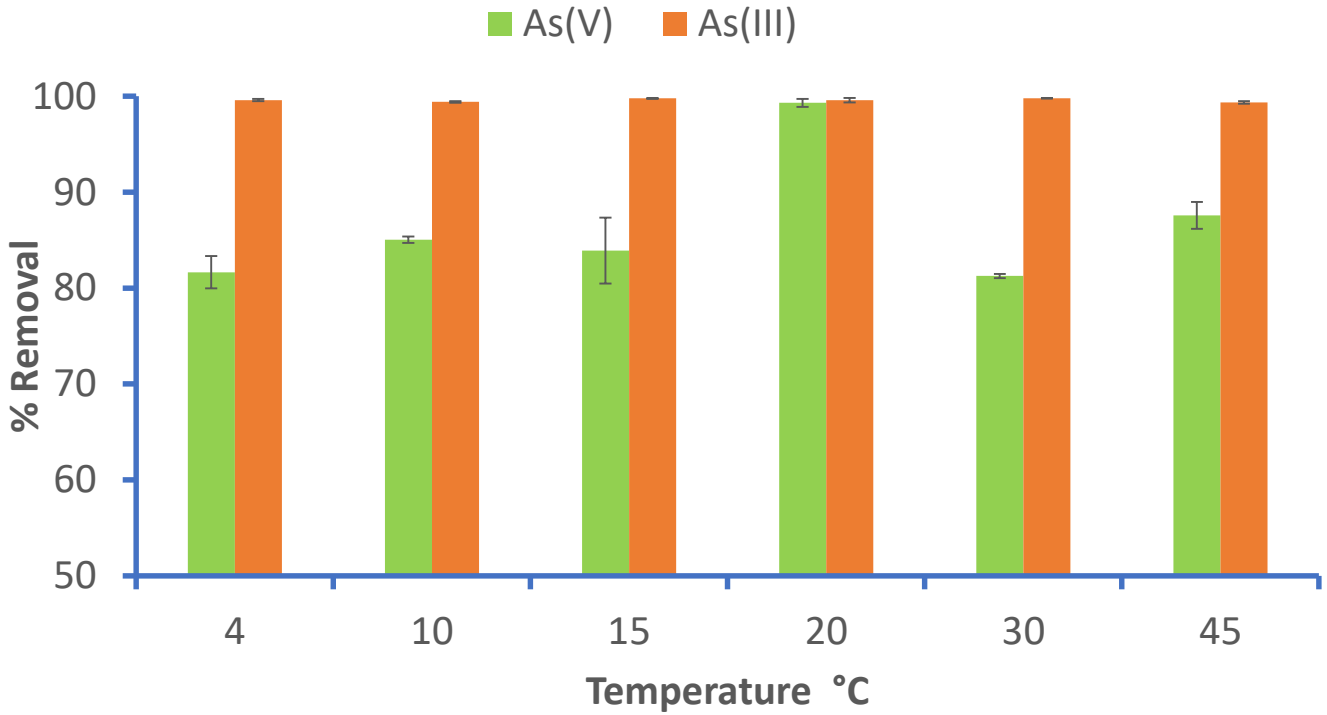
STEM−EDS elemental mappings of Fe−As reactions at three resolutions: (1, 7, and 13) HAADF images, (2, 8, and 14) Fe, (3, 9, and 15) O, (4, 10, and 16) As, (5, 11, and 17) Fe and As, and (6, 12, and 18) Fe, As, and O

Ling and Zhang, 2014

Removal in mixture of AS(V) & As(III)



Temperature effects



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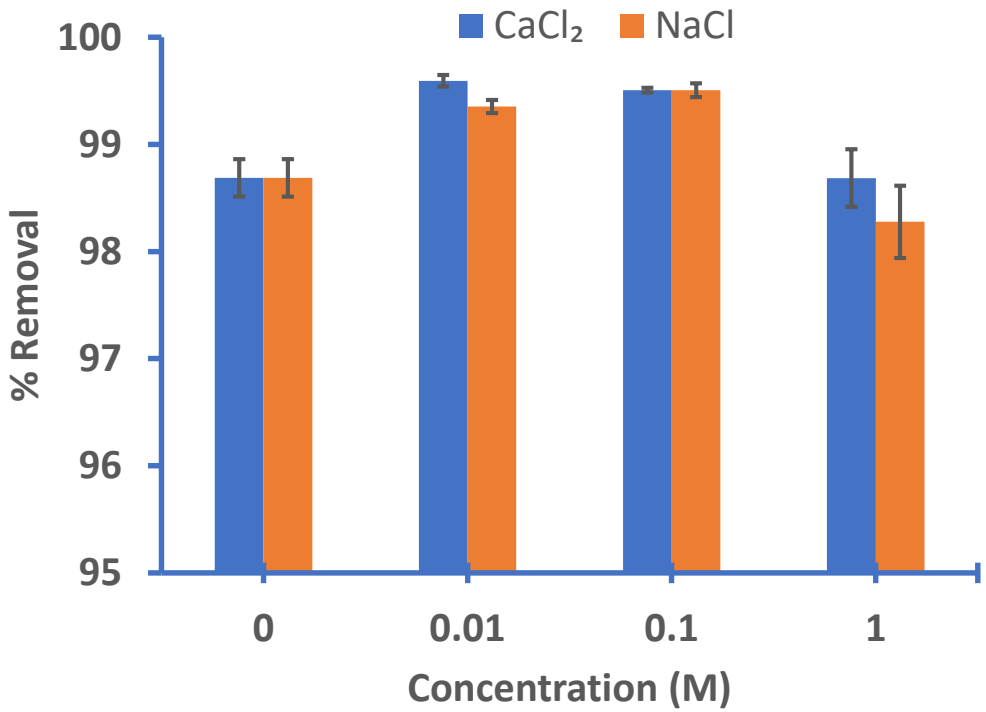
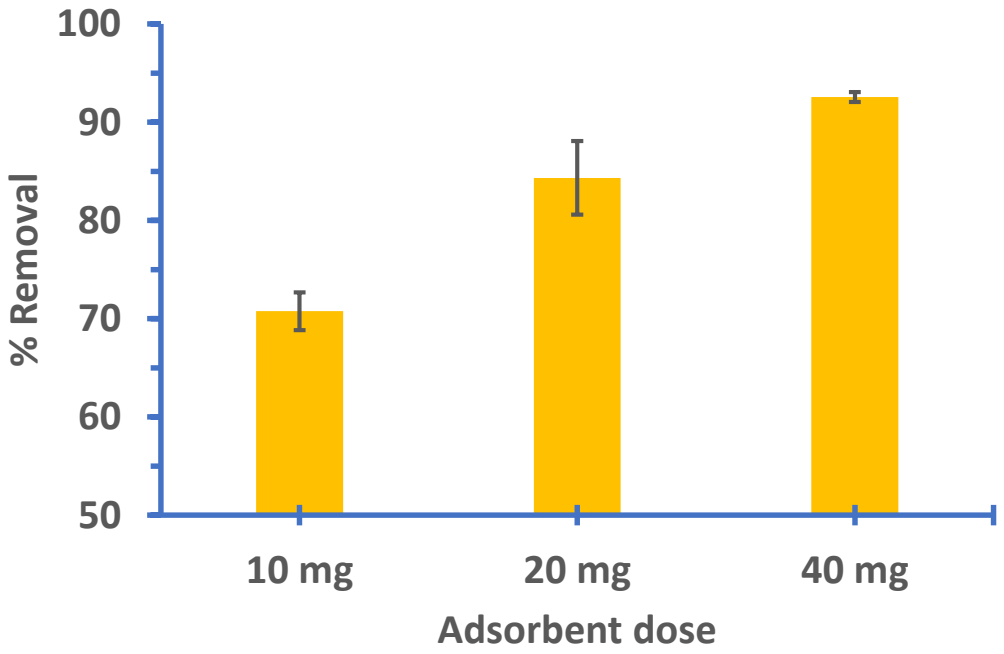
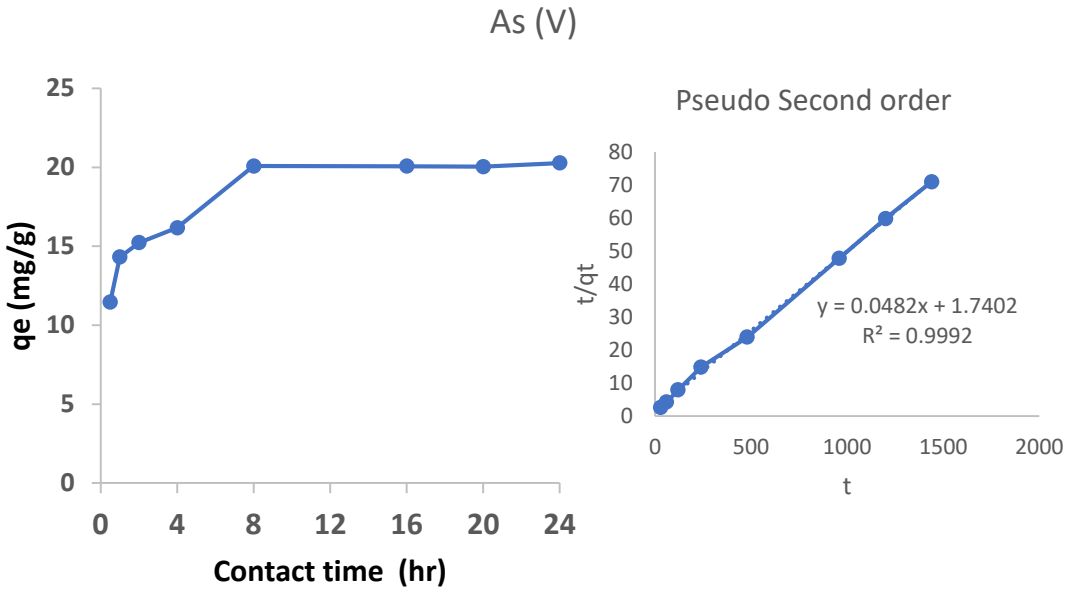
Arsenate [As(V)] removal by GNZVI hybrid (C_0 = 5 mg/L)

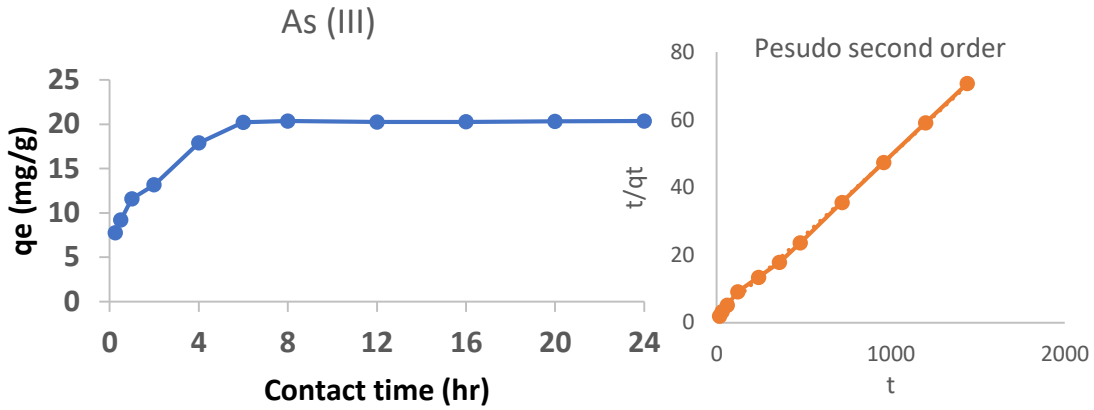


Arsenate [As(V)] removal by GNZVI hybrid (C_0 = 5 mg/L, Contact time: 30 mins)



Reaction Kinetics





		Pseudo 1st order			Pseudo 2nd order		
	Exp qe	qe cal	R^2	K1	qe cal	R^2	K
As (V)	20.27	6.13	0.772	0.0005	**20.75**	**0.999**	**1.3×10^{-3}**
As(III)	20.35	5.85	0.662	0.0041	**21.05**	**0.999**	**3.3×10^{-4}**

Arsenic Contamination- Public Health

- Arsenic Group 1 Carcinogen (WHO)
- > 300 million worldwide.
- 13 million : USA; 70 million : Bangladesh (Murcott 2012).
- **Acute effects:** vomiting, abdominal pain and diarrhea lead to numbness and tingling of the extremities, muscle cramping and death
- **Long-term effects:** skin lesions precursor to skin cancer, cancers of the bladder and lungs, developmental effects, neurotoxicity, diabetes, pulmonary disease and cardiovascular disease, adverse pregnancy outcomes and infant mortality, with impacts on child health

Information

- Reduction potential of nZVI & As(V)-to-As(0) −0.447 V (Fe/Fe(II)), and . 0.499 V. The reduction of As(V) thermodynamically possible
- The first step in removing arsenic from water entails the convective transfer and/or molecular diffusion of dissolved arsenate from the bulk solution to the nZVI−water interface. Arsenate is attracted to the surface by electrostatic interactions as both arsenate and the iron surface are charged, and via ligand exchange that replaces a surface-bonded -OH group (>Fe−OH) with an arsenate ion. This constitutes the outer ring observed on the arsenic mapping. The surface-bound As(V) continues to diffuse through the surface layer. Further penetration or diffusion of As(V) is induced by its reduction to As(III) and As(0), and the latter accumulates at the Fe(0)− oxide interface
- Fe(III) oxide near the particle−water interface to mixed Fe(II)/Fe(III) oxides close to the core. The surface of the oxide layer contains hydroxide groups after being exposed to water and has acid−base chemistry similar to that of iron oxides in water. Measurements show that the nZVI has a zerocharge pH or pHzpc at ∼8.2 Thus, it can attract and/or adsorb As(V) or As(III) via electrostatic attractions or ligand exchanges that replace surface-bonded OH groups (>Fe−OH) with arsenate ions.
- The presence of oxygen vacancies and lattice disorder could give arise to elevated charge transfer and ionic mobility at room temperature.
- For nZVI, the maximum As(III) loading capacity is 2.2 mM As/g, while the value of the oxides is no more than 0.17 mM As/g. As a firstorder estimate in which we consider that the average As(III) adsorption density on an iron oxide surface is ∼3 sites/nm2 , 13 one can estimate that the maximum As(III) uptake by the iron oxides is ∼0.2 mM As/g, which is consistent with the experimentally observed capacities. On the other hand, the capacity of arsenite removal by nZVI is well in excess of the total surface adsorption sites available, indicating that arsenite was not retained as merely a surface adsorbed layer