

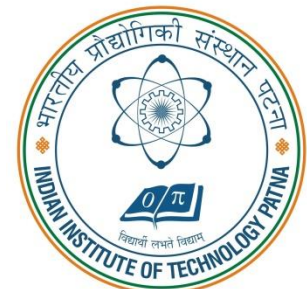
Impregnation of metal based oxides within granular activated carbon for removal of inorganic contaminants

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Inorganic contaminant: Arsenic & Fluoride in drinking water

- More than **100 million people** are affected by arsenic (standard limit: $50 \mu\text{g L}^{-1}$) in Bangladesh and India. [Smedley and Kinniburgh (2002), Appl. Geochem.]
- 'Arsenic contamination in Bangladesh is the **largest poisoning** of population in **human history**' [Smith et al (2000), Bulletin WHO]
- **Millions of people** consume fluoride contaminated drinking water (concentration exceeding 1.5 mg/L) daily.
- In India, several states such as **Andhra Pradesh, Rajasthan and Gujarat** — are severely affected by fluoride contamination.
- In recent times, fluoride contamination in water is also detected at various locations in **Assam, West Bengal, Haryana, Madhya Pradesh, Maharashtra and Karnataka** [Bhatnagar et al., 2011; Rajnarayan et al., 2012]

Objectives

Hypothesis: Combining high specific surface area of AC with adsorption active sites of metal oxides: enhance the efficiency of the composite for removal of inorganic contaminants such as arsenic & fluoride

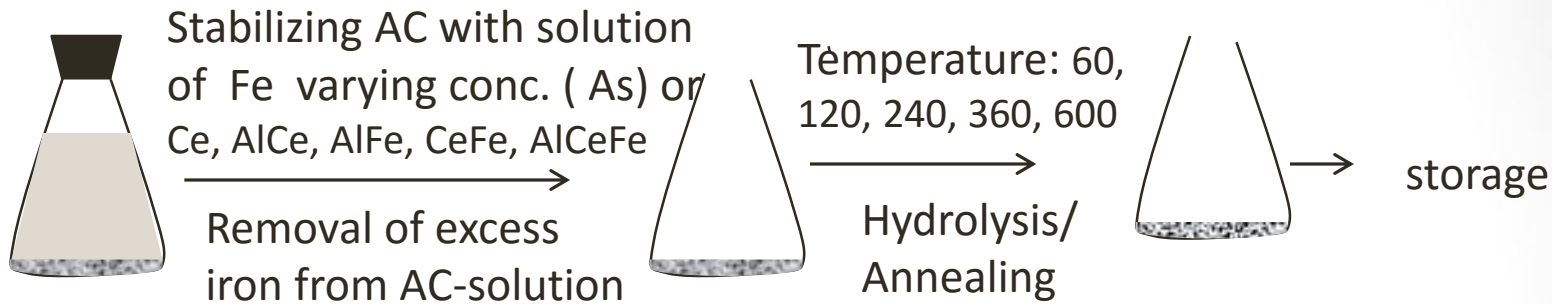
Objective-1: Evaluation of arsenic removal efficiency by the iron impregnated activated carbon (AC-Fe) composites

Objective-2: Evaluation of fluoride removal efficiency by the metal (Al, Ce & Fe) impregnated activated carbon (AC-M) composites

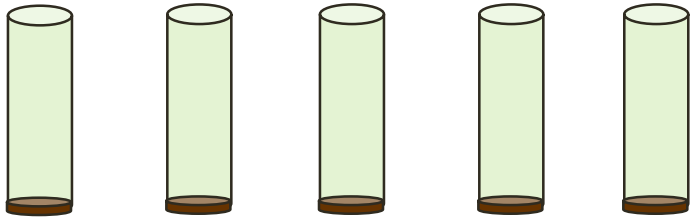
Specific Objectives

- Synthesis AC-M composites under varying reaction conditions
- Estimate the arsenic & fluoride removal efficiency by the composites and identify the best composite
- Assessment of sorption behavior (isotherm and kinetics) of arsenic & fluoride by the selected composite
- Effect of solution chemistry on removal of arsenic & fluoride

Synthesis of AC-M composite & Batch experiments



Preparation of AC-M composites



As & F removal efficiency

Volume of solution = 50 mL
Concentration of F = 10 mg/L, As = mg/L
Mass of AC-M = 0.1 g (2 g/L)
Time: 3 h or 24 h

Batch experiment: fluoride removal behavior

Adsorption behavior

Volume of solution (50 mL)
Mass of AC-M: 2 g/L

Isotherm test:

Concentration of F: 5 mg/L-50 mg/L
Time: 15 h (F) or 24 h (As)

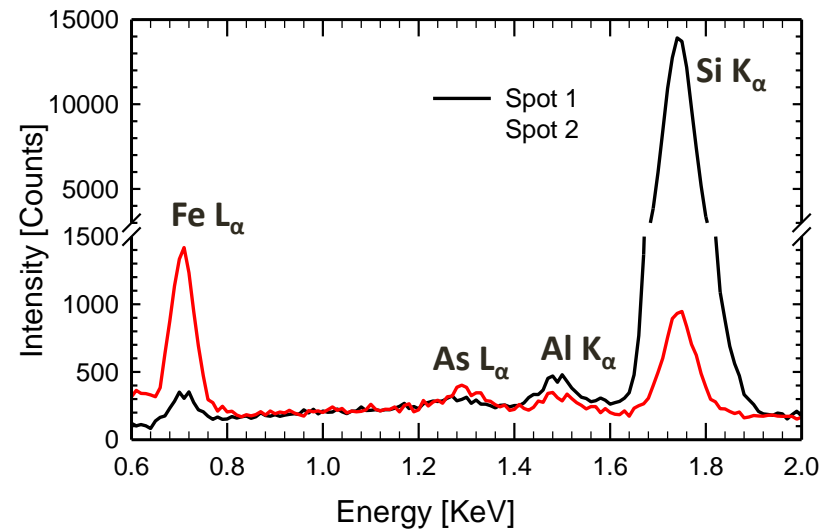
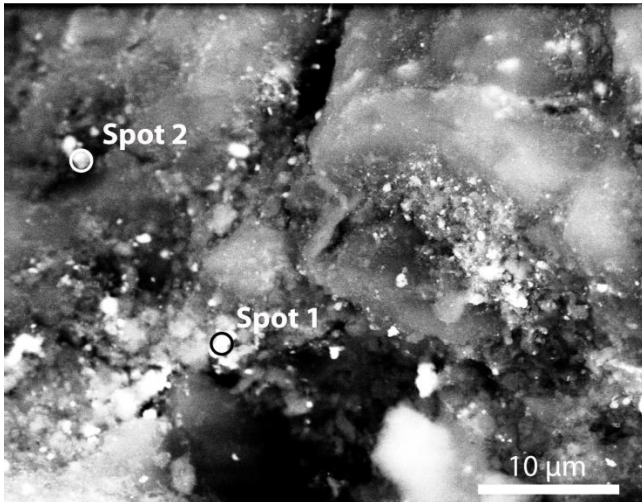
Fluoride removal by different composite: No of AC-M composites=25
Effect of co-ions : 0– 50 mM (sulfate, phosphate)
Effect of pH: 4-10

kinetics test:

Concentration of F: 10 mg/L, As = mg/L
Time: Fluoride: 5 min- 3 h , Arsenic: 5min-5 h (15h - 72 h)

Arsenic removal by AC-Fe composite

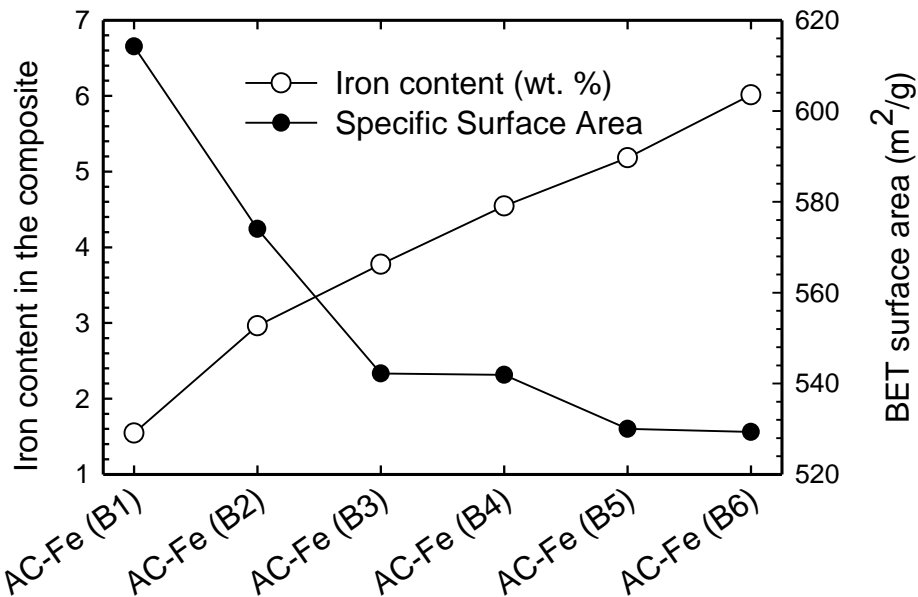
- Adsorption of arsenic:



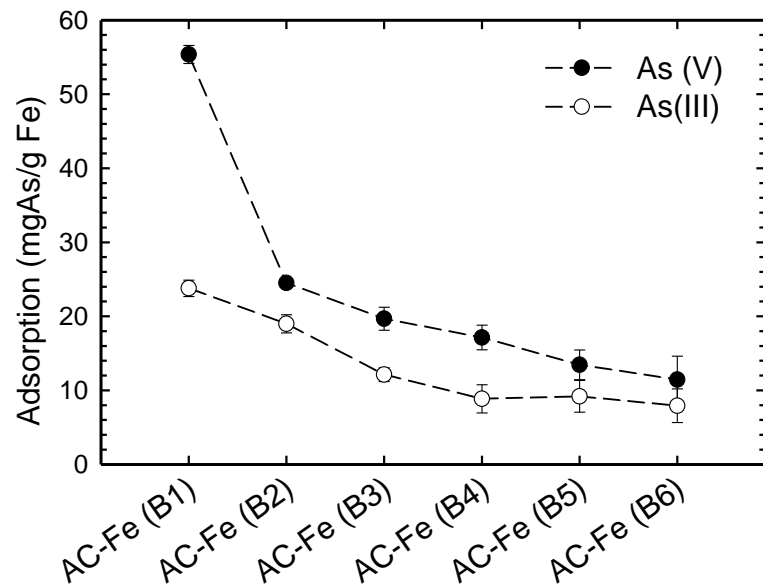
- Fe-hydr(oxide) is impregnated in amorphous form
- Arsenic is identified in the composite, where iron is also present
- As is not associated with other mineral impurities in AC
- As removal increases significantly with iron impregnation

Removal of arsenic is mainly governed by adsorption mechanism and iron(hydr)oxide surface in AC is the most active site for As adsorption

Arsenic adsorption by AC-Fe containing different amount of iron



Different AC-Fe composites

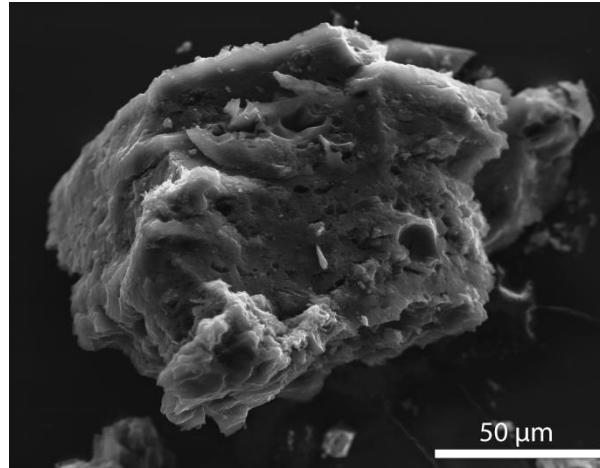
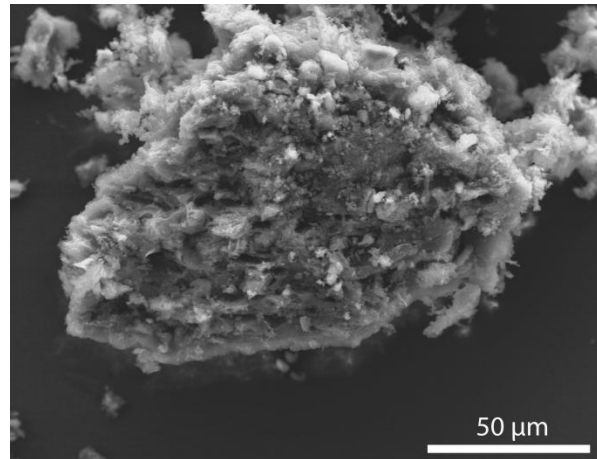


Different AC-Fe composites

- AC-Fe (B1) contain lowest iron: 1.54 % & AC-Fe (B6) highest iron: 6%
- With increase in iron content, SSA of composite decreases
- With increase in iron content, arsenic adsorption capacity decreases

Excess iron resulted in reduction in SSA possibly due to pore blocking in the AC-Fe composite

Iron and arsenic distribution on and within activated carbon

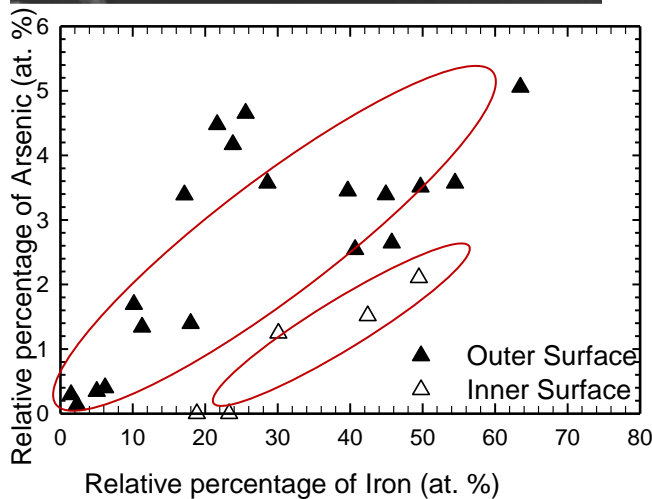


AC-Fe (B1)

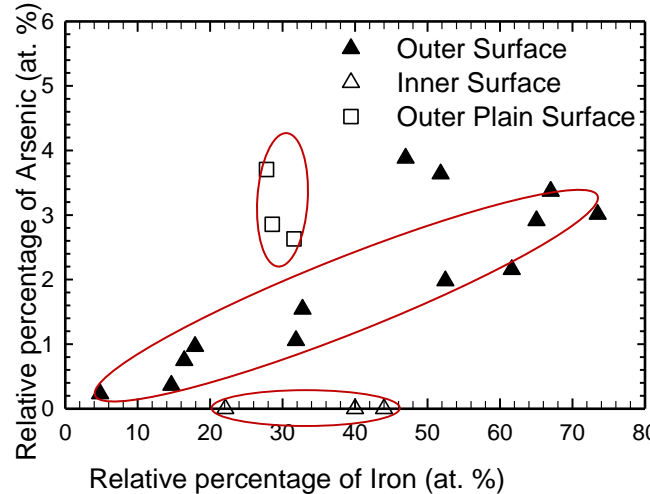
- Increasing trend in As (relative %) with iron at both outer and inner surface

AC-Fe (B6)

- At inner surface negligible As at some locations where iron is present
- At outer (rough) surface similar trend as AC-Fe (B1)
- At smooth outer phase, As increases irrespective of iron content



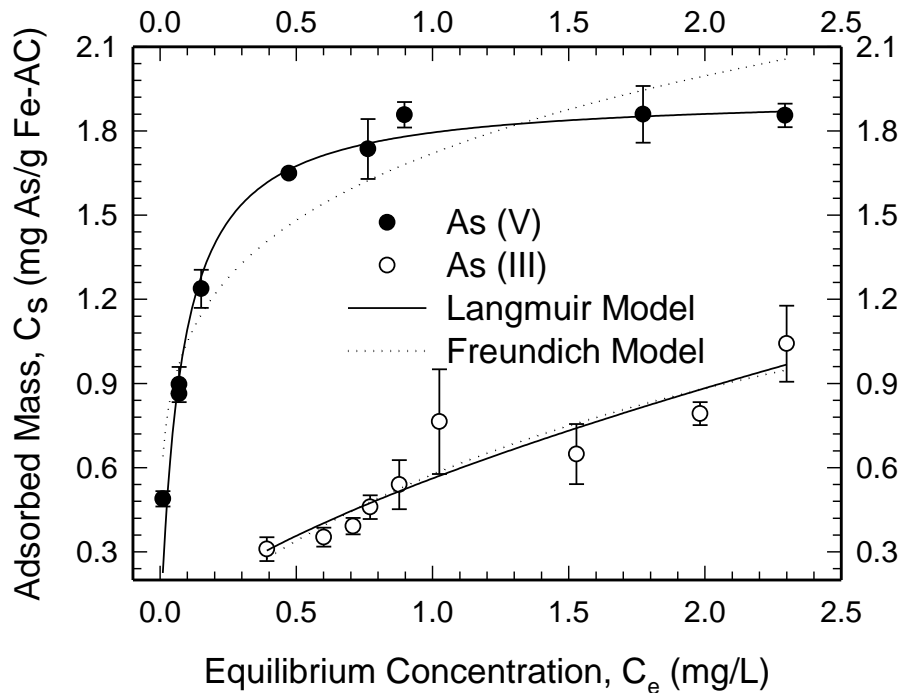
AC-Fe (B1): Lowest Fe (1.54%)



AC-Fe (B6): Highest Fe (6%)

Small amount of iron distributed uniformly within activated carbon without significant pore blocking, resulted in most efficient As adsorption capacity

Adsorption isotherm: AC-Fe (B1)



$$c_s = k_f c_e^{1/n} \quad \text{Freundlich model}$$

$$c_s = \frac{q_m k_l c_e}{1 + k_l c_e} \quad \text{Langmuir model}$$

$$\Delta G = -RT \ln k_l \quad \text{Energy release due to adsorption}$$

c_s : Adsorbed mass per unit adsorbent at equil.

c_e : arsenic concentration in solution at equil.

k_f : Freundlich adsorption coefficient

q_m : maximum adsorption capacity

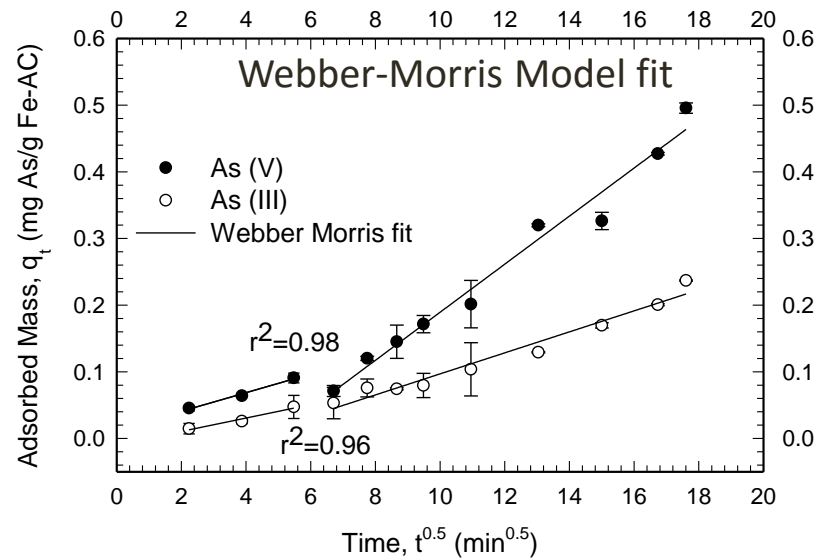
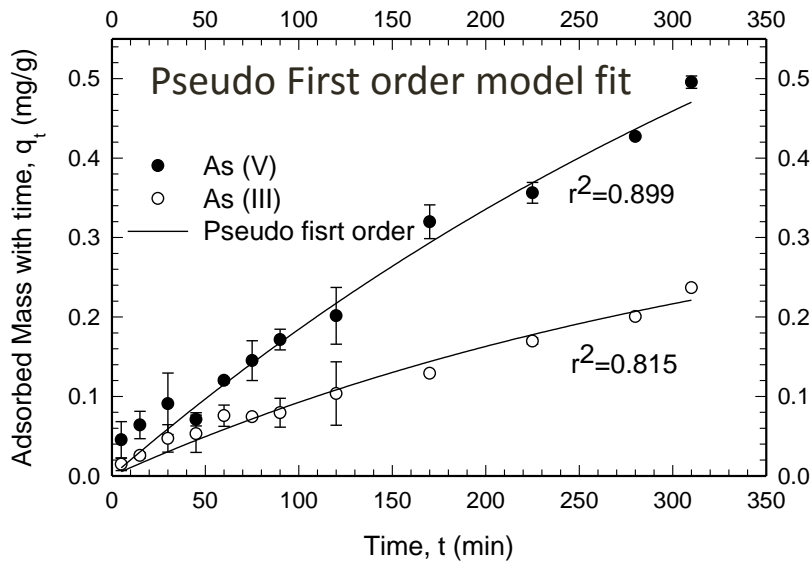
k_l : Langmuir adsorption coefficient

R: ideal gas constant, T: Temperature,

Adsorption Isotherm

Freundlich		Langmuir				
	1/n	r_f^2	q_m [mg/g AC-Fe]	q_m [mg/g Fe]	ΔG kJ mol ⁻¹	r_l^2
As (V)	0.25	0.94	1.93	125	-3.40	0.99
As (III)	0.67	0.88	1.52	98.4	-0.39	0.89

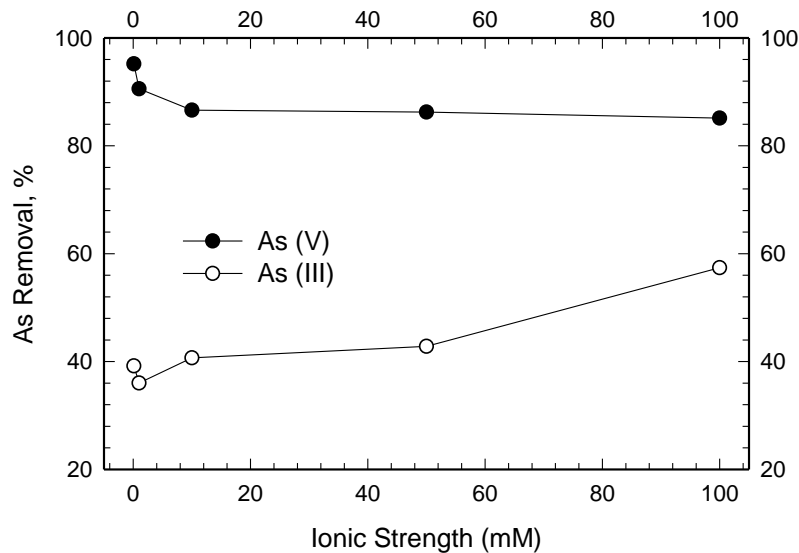
Adsorption Kinetics: AC-Fe (B1)



	Pseudo first order		Pseudo second order		Webber Morris Model	
	k_t (h^{-1})	r_{ft}^2	k'_t ($g\ mg^{-1}\ h^{-1}$)	r_{st}^2	$k''_{t(t=0:30)}$ ($mg\ g^{-1}\ min^{-0.5}$)	$k''_{t(t>30)}$ ($mg\ g^{-1}\ min^{-0.5}$)
As (V)	0.432	0.90	0.78	0.75	0.014	0.037
As (III)	0.420	0.82	0.12	0.48	0.010	0.016

Pseudo first order model can explain the kinetics data better than pseudo second order model

Effect of ionic strength on arsenic removal

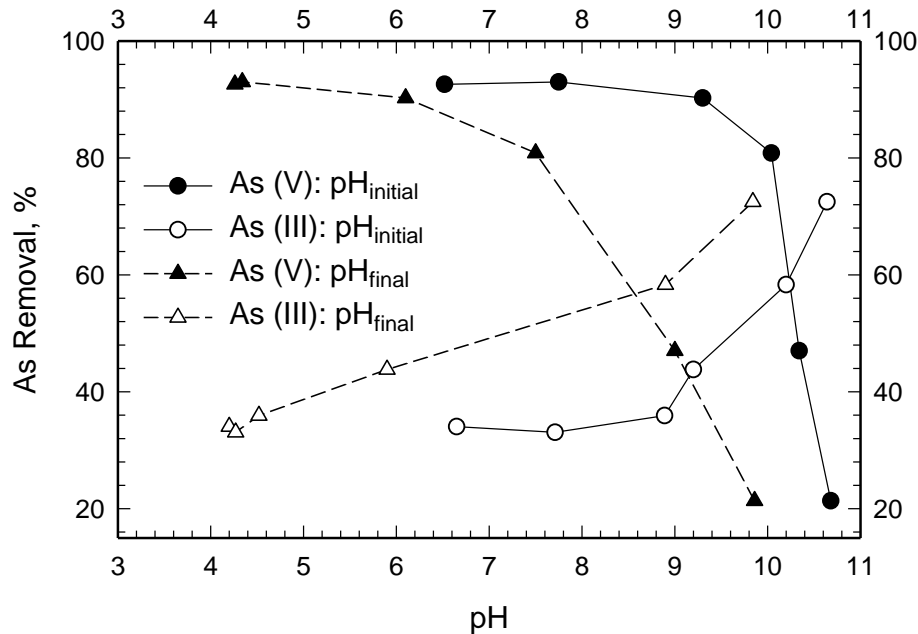


- Removal of As (V) does not change much (<10%) with NaCl concentration (range: 0.1-100 mM)
- Removal of As (III) increases beyond 50 mM NaCl

Trend in As (V) and As (III) removal indicates

- Inner sphere surface complexes is most likely surface interaction mechanism (Goldberg and Johnson 2001)
- Ion- exchange is probably not very relevant in this system

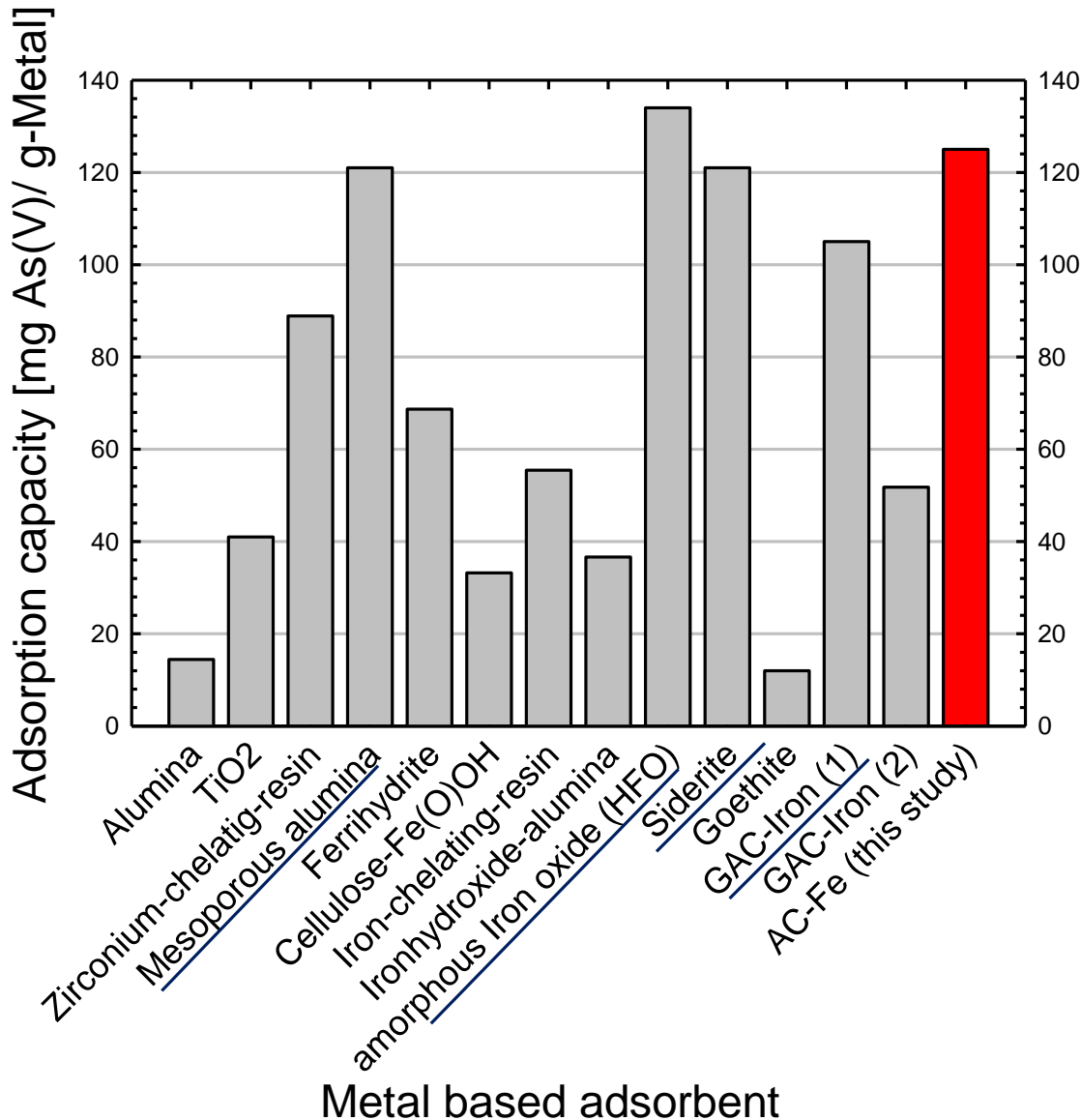
Effect of pH on arsenic removal



- pH of the system changes and reaches near equilibrium after 30 min; both initial and final pH is indicated
- Removal of As (V) decreases with increase in pH, in the pH_{final} range of 4-10
- Removal of As (III) increases with pH, in the range of 4-10

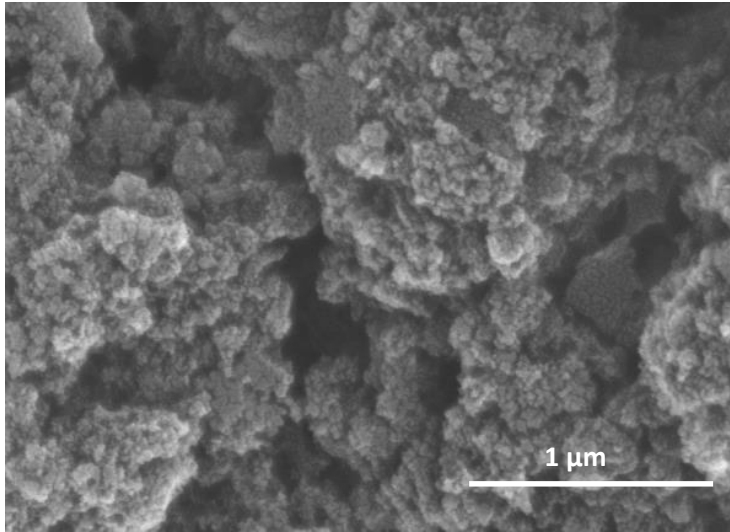
Occurrence of different species of As (V) and As (III) and formation of different surface complexes with iron at various pH is responsible for this behavior.

Comparison of As removal efficiencies

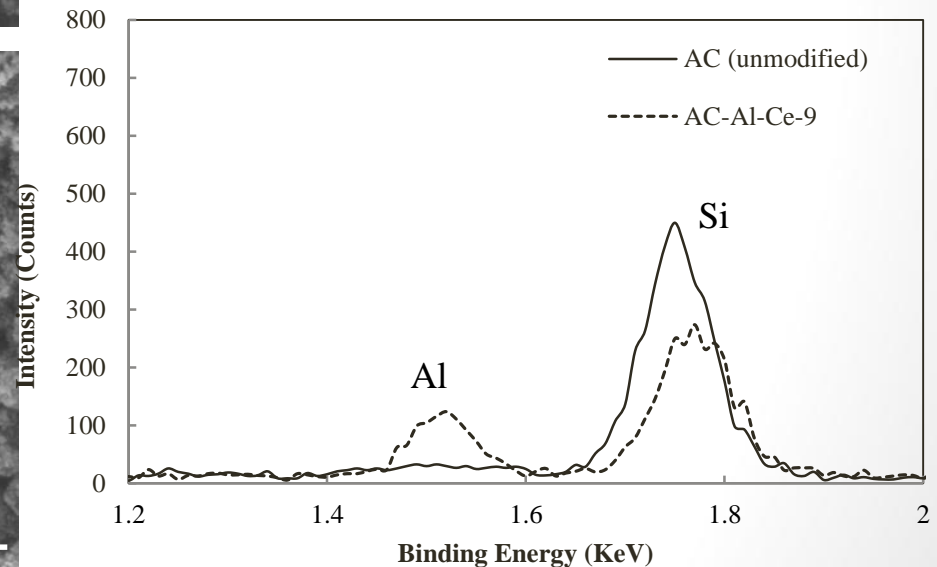
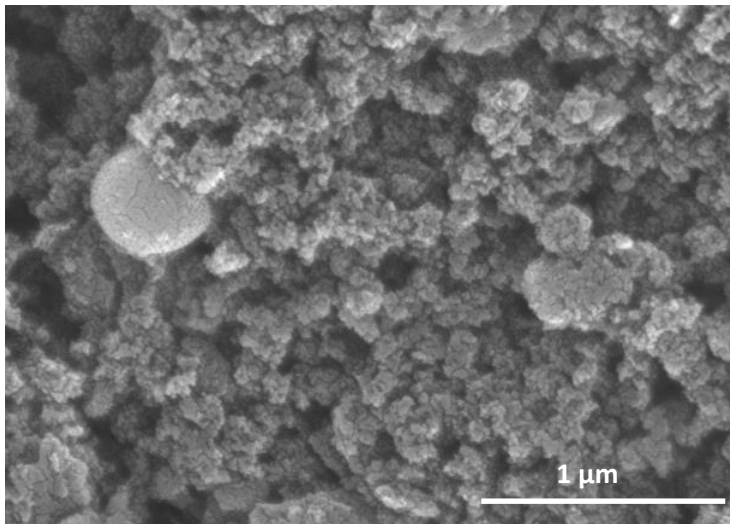


- For presented data:
Reported pH range of 5-8.
- Few adsorbent exhibit very high As (V) adsorption capacity (>120 mg/g)
- As(V) removal capacity by Fe-(hydr)oxide in this study is in the higher range (125 mg/g)
- Differences in As adsorption by GAC-Iron with similar range of SSA depends on type of GAC used, synthesis condition and formation of multiple iron-oxide/hydroxide complex

Characterization of the AC-M composite synthesize for Fluoride removal

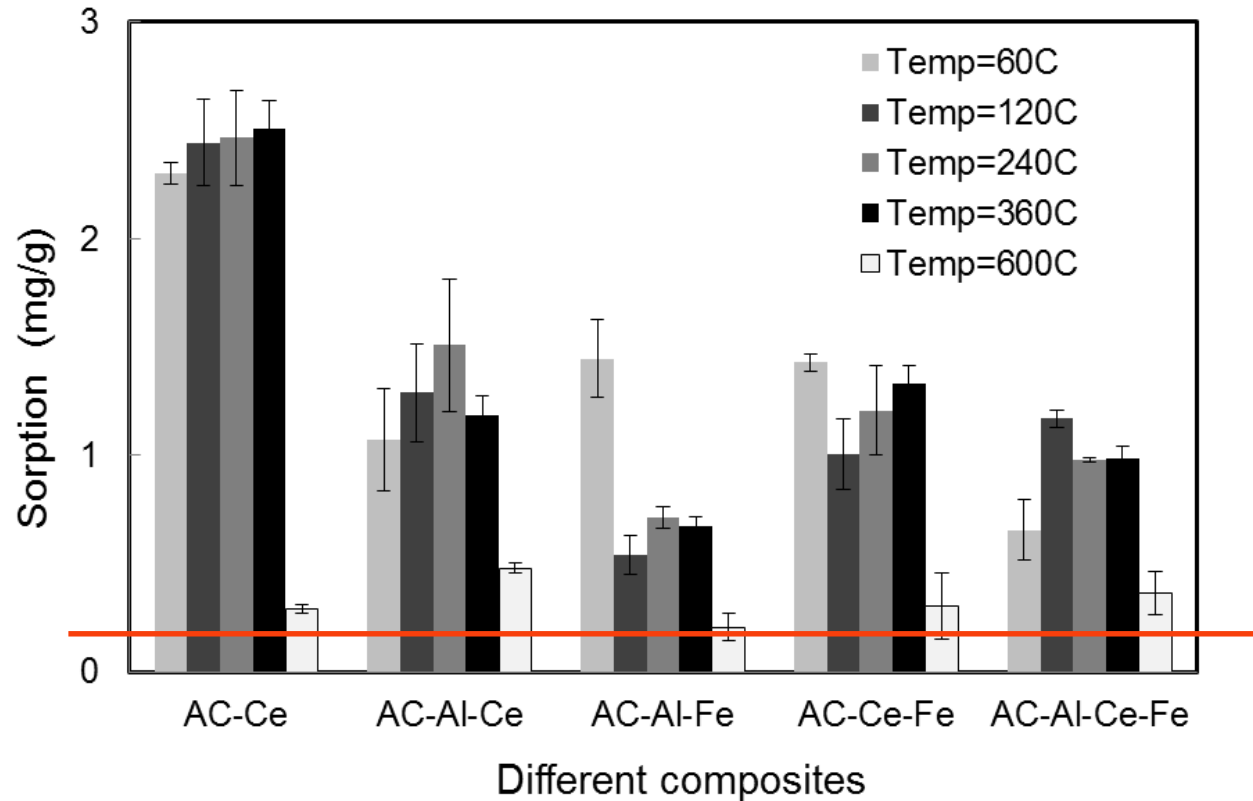


- SEM imaging: The metal oxides/hydroxides are not visible as crystalline structure
- Chemical analysis: indicates presence of impregnated metal within AC. They are likely to be present as of amorphous structure)



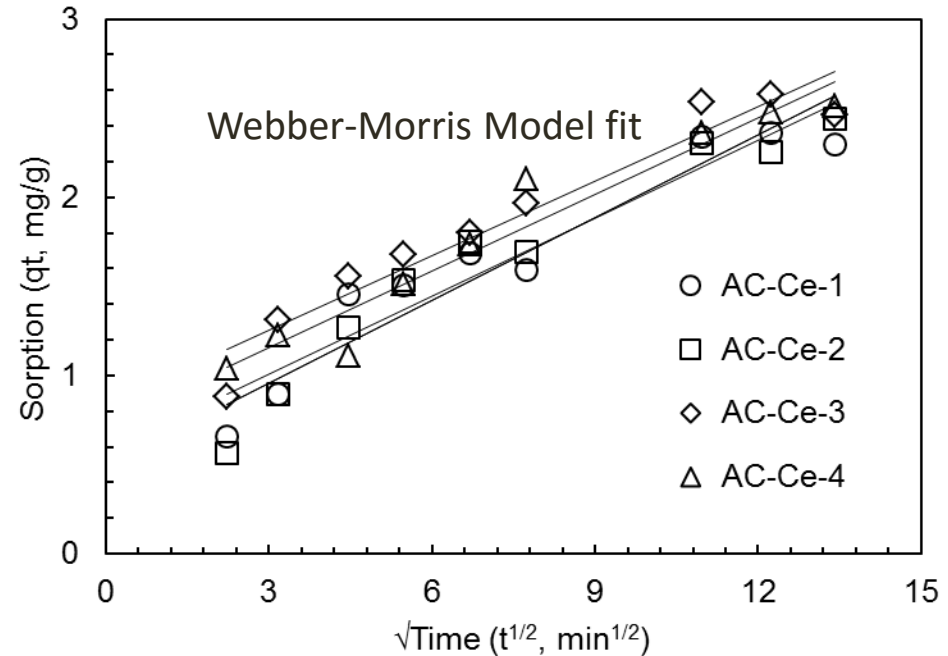
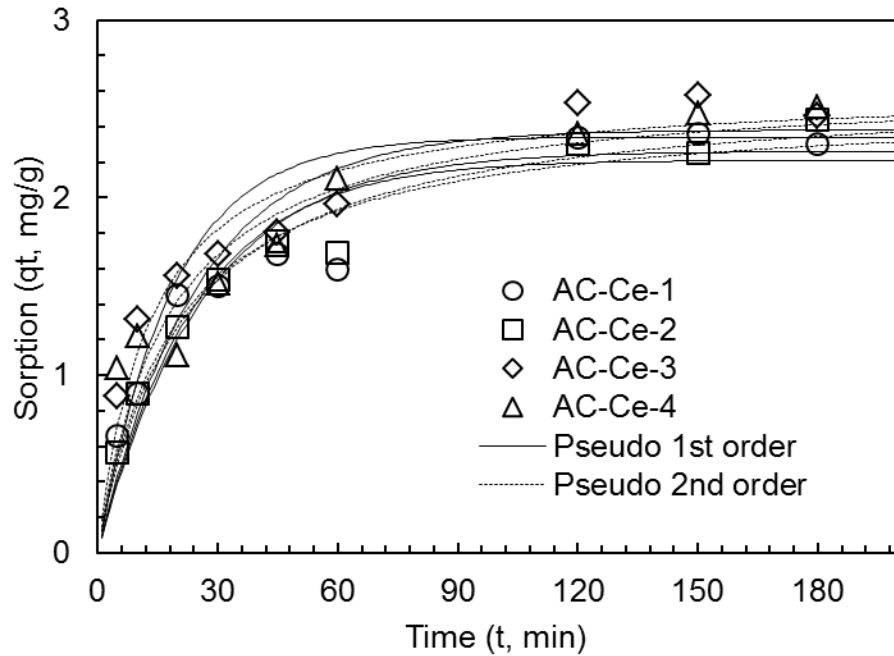
SEM image of AC-AlCe composite (ARCI, Hyderbd)

Fluoride removal by different AC-Metal composites



- AC can sorb 0.18 mg/g of fluoride in the given condition (fluoride C= 10 mg/L)
- Impregnation of metal can improve the performance of the composite significantly
- Impregnation of Ce shows the best performance which can sorb 2.5 mg/g of fluoride
- Impregnation of other metal (i.e., Al, Fe) along with Ce reduces the performances especially the concentration and molar ratio used in this study (due to dissolution of Al)
- Temperature ranging from 60°C to 360°C does not have much effect on fluoride removal
- Fluoride removal efficiency reduced sharply at a synthesis temperature of 600 °C

Fluoride sorption kinetics by AC-Ce composites

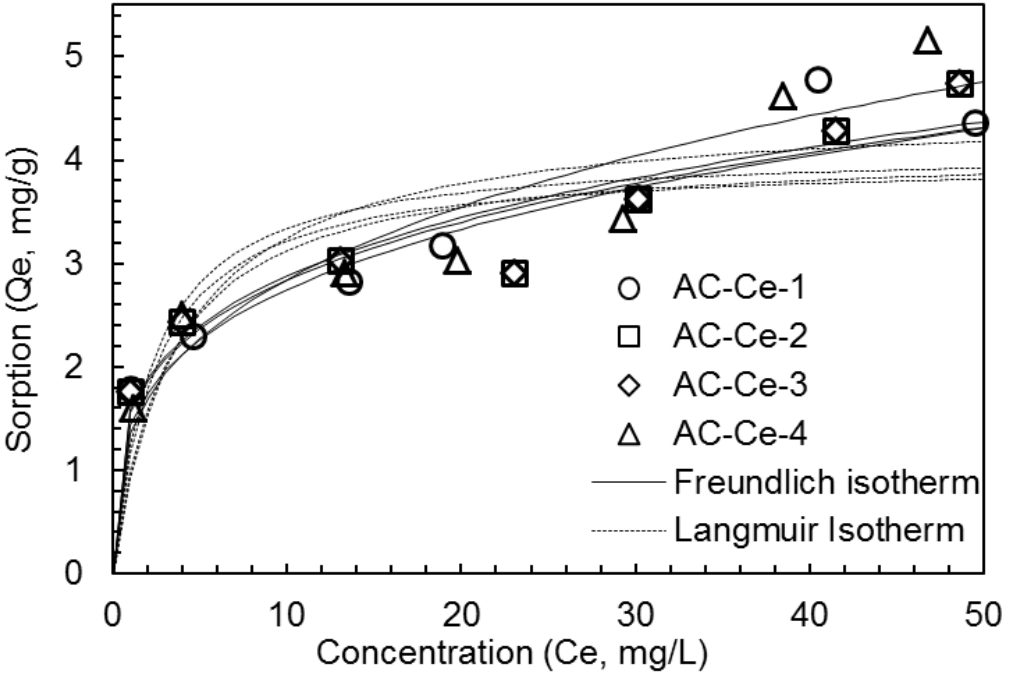


- Pseudo second order kinetics can explain the model better than first order kinetics
- Linear relationship between q_t vs \sqrt{t} is observed (with $r^2 > 0.91$)
- Rate limiting factors are probably controlled by both inter-particle diffusion as well as boundary layer diffusion

• **Rate of sorption is reasonably high**

Samples	Pseudo second order			Weber-Morris model	
	q_e (mg/g)	k'_t (1/min)	r_{st}^2	$k''t$ (mg/g/ $\text{min}^{1/2}$)	r_{st}^2
AC-Ce-1	2.53	0.021	0.93	0.15	0.91
AC-Ce-2	2.62	0.018	0.97	0.15	0.93
AC-Ce-3	2.62	0.029	0.92	0.14	0.93
AC-Ce-4	2.64	0.022	0.84	0.14	0.94

Fluoride adsorption isotherm by AC-Ce composites



$c_s = k_f c_e^{1/n}$ Freundlich model

$c_s = \frac{q_m k_l c_e}{1 + k_l c_e}$ Langmuir model

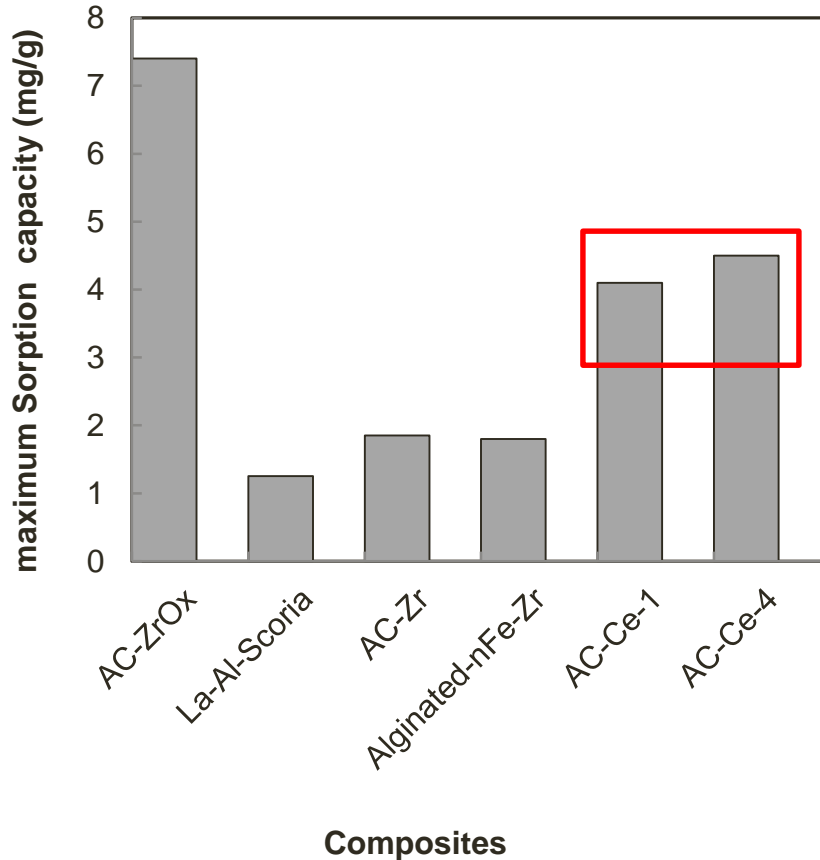
q_s : Adsorbed mass per unit adsorbent at equil.
 c_e : arsenic concentration in solution at equil.
 k_f : Freundlich adsorption coefficient
 q_m : maximum adsorption capacity
 k_l : Langmuir adsorption coefficient

- Freundlich isotherm explain the data better than Langmuir isotherm
- Suggests the composite has heterogeneous sorption sites. and monolayer sorption is probably not relevant

Samples	Freundlich model			Langmuir model		
	k_f	$1/n$	r_f^2	q_{max} (mg/g)	k_l	r_l^2
AC-Ce-1	1.44	0.28	0.82	4.1	0.32	0.59
AC-Ce-2	1.58	0.26	0.89	4.1	0.44	0.68
AC-Ce-3	1.56	0.26	0.83	4.0	0.41	0.72
AC-Ce-4	1.36	0.32	0.87	4.5	0.26	0.68

- Better sorption at lower concentration ($1/n < 1$)
- Maximum sorption capacity by AC-Ce-4 is 4.5 mg/g.

Comparison of Fluoride removal efficiencies



- Reported value of Fluoride sorption by different metal hydroxides impregnated composite is in the range of 1.25 mg/g to 1.85 mg/g
- Sorption by AC-Zr-oxide is reported in the range of 7.4 mg/g
- In this study the max sorption is in the range of 4.1-4.6 mg/g, which is reasonably high

Velanzuage-Jimenez et al 2014

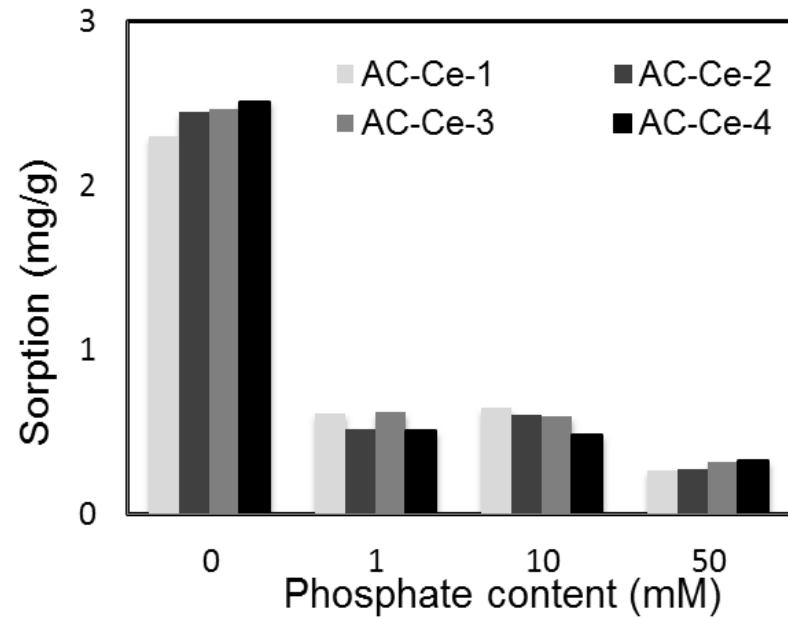
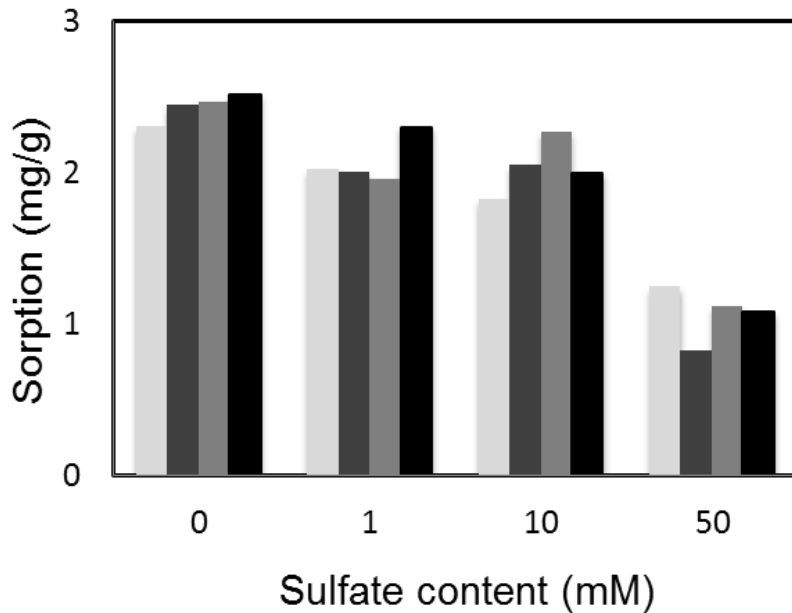
Bharati et al. 2014

Zhang et al 2014

Velanzuage-Jimenez et al 2014

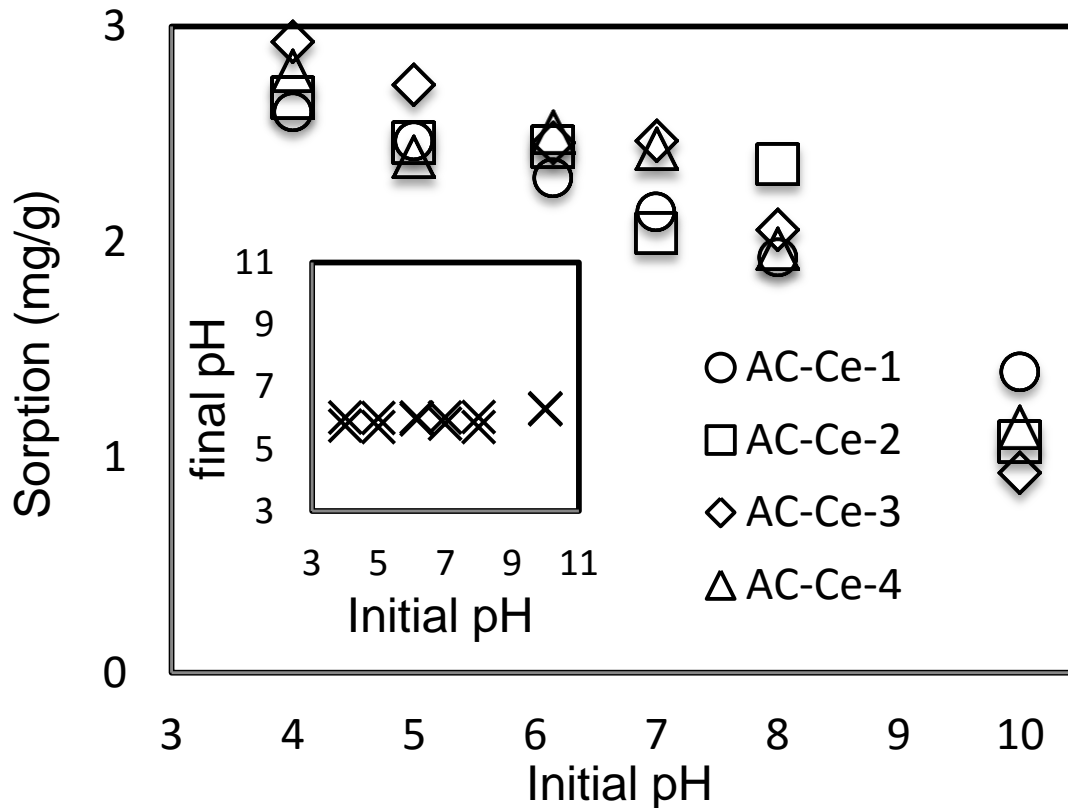
Swain et al. 2013

Effect of co-ions on fluoride removal



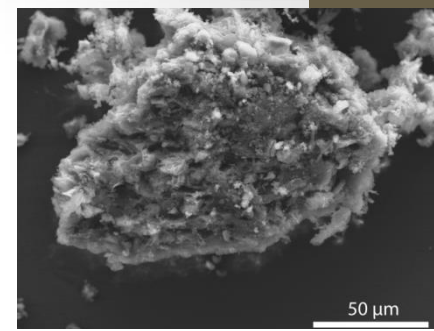
- With increase in sulfate concentration from 0-10 mM, not much change in fluoride removal is observed
- At 50mM sulfate concentration fluoride removal decreases from approximately 2.5 mg/g to 1.2 mg/g
- Presence of small amount of phosphate (1mM) decreases the fluoride removal efficiency almost 5 times (2.5 mg/g to 0.5 mg/g)
- Possible reason/ mechanism is probably release of OH^- ions and competition for sorption sites

Effect of pH on fluoride removal

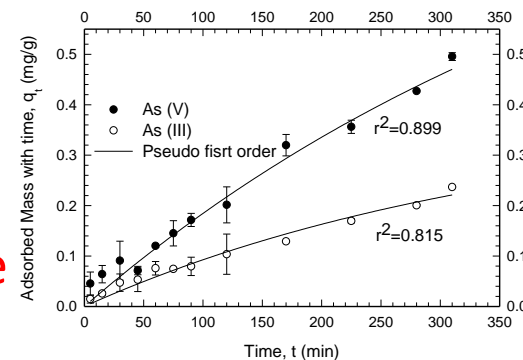
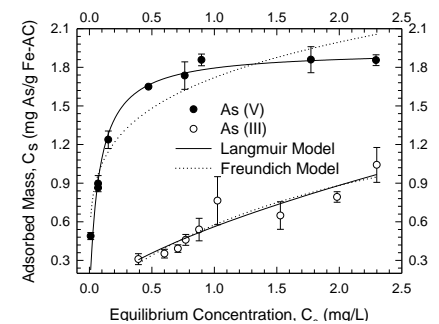
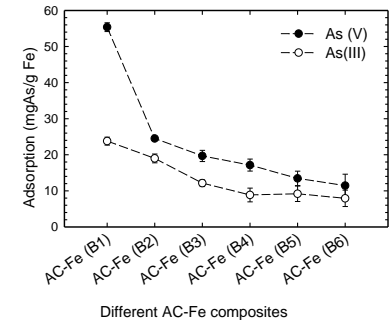


- At around pH 4 maximum fluoride removal (approximately 3 mg/g) was observed
- With increase in pH fluoride removal efficiency decreases
- At pH 10 the fluoride removal efficiency decreases sharply to around 1 mg/g
- The composite has buffering effect and the pH at the equilibrium reaches around 6

Conclusion

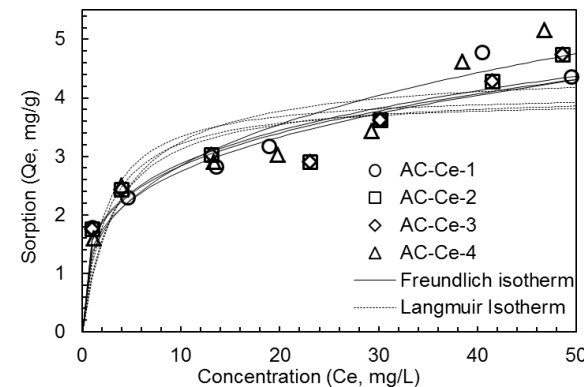
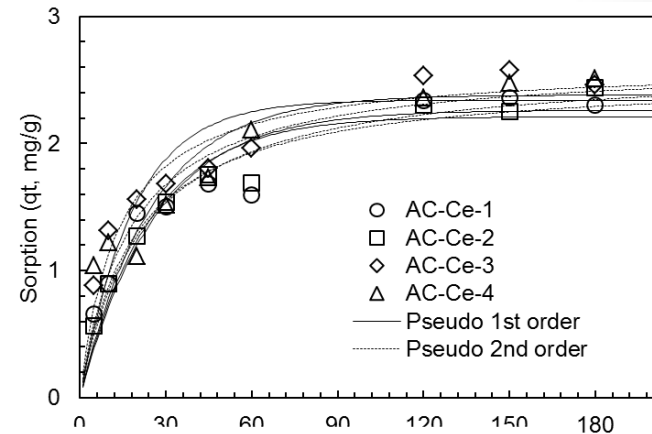
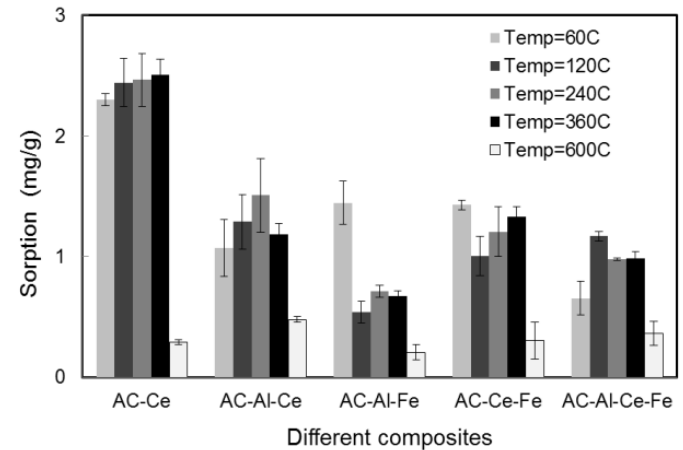


- A small amount of iron impregnated in activated carbon can increase arsenic removal significantly compared to unmodified AC
 - ❑ As (III) removal increase from **17%** (AC) to **61%** [AC-Fe (B1)]
 - ❑ As (V) removal increase from **19%** (AC) to over **99%** [AC-Fe (B1)]
- Excess amount of iron can reduce the performance of the composite due to heterogeneous distribution of iron and pore blocking
- Langmuir isotherm can explain the adsorption behavior most efficiently: Maximum adsorption capacities: 125 mg As (V)/ gFe and 98.4 mg As (III)/g Fe
- Pseudo first order model can explain the kinetics data better within 5 hours time span
- Overall AC-Fe composite shows promising performance for As removal



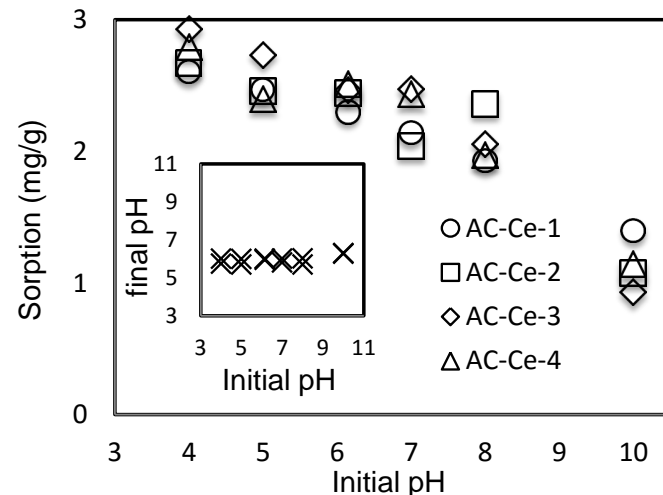
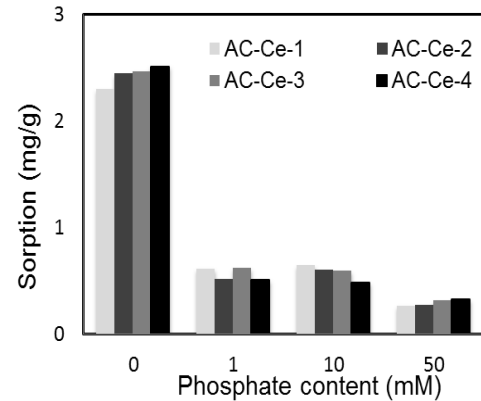
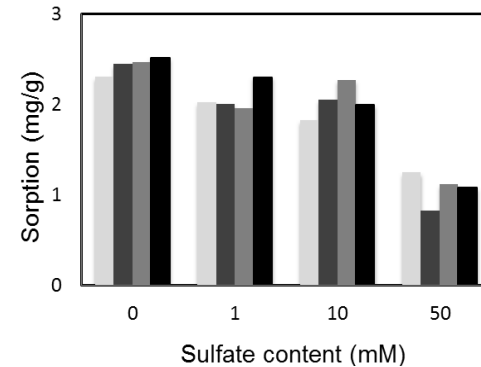
Conclusion

- A small amount of cerium (Ce) impregnated in activated carbon can increase fluoride removal efficiency significantly (0.18 mg/g to 2.5 mg/g)
- All the AC-Ce composite (except the one synthesized at 600°C) shows similar sorption behavior
- Pseudo second order model can explain the kinetics data better within 3 hours time span, with high rate of sorption
- Freundlich isotherm can explain the adsorption behavior better



Conclusion

- Phosphate concentration has a more significant effect on fluoride removal compared to sulfate concentration
- Increase in solution pH decreases the performance of composite.
- **High fluoride sorption at low fluoride concentration, fast rate of sorption and buffering effect can make it suitable for using it as filter material for removing fluoride from drinking water**



Thank you

