Supporting Information

Core-shell structured Zero-valent Manganese (ZVM): A novel nanoadsorbent for efficient removal of As(III) and As(V) from drinking water

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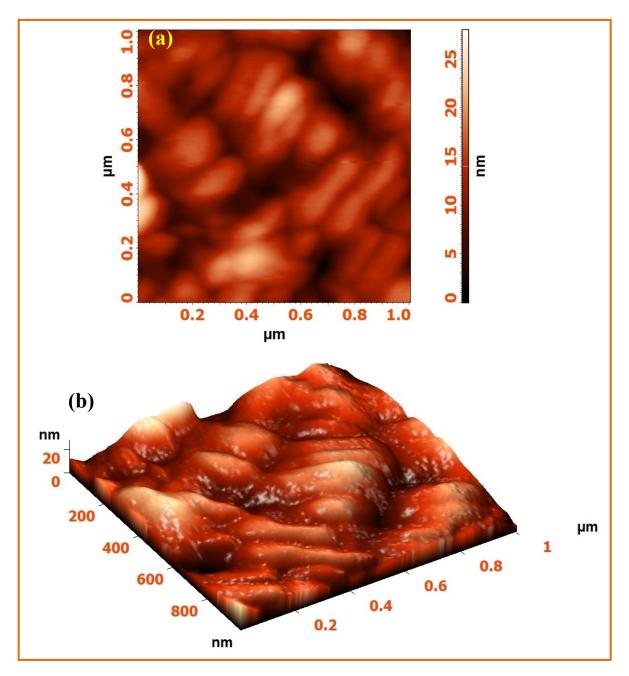


Fig. S1. Atomic force microscope image of ZVM surface: (a) 2-D view (b) 3-D view.

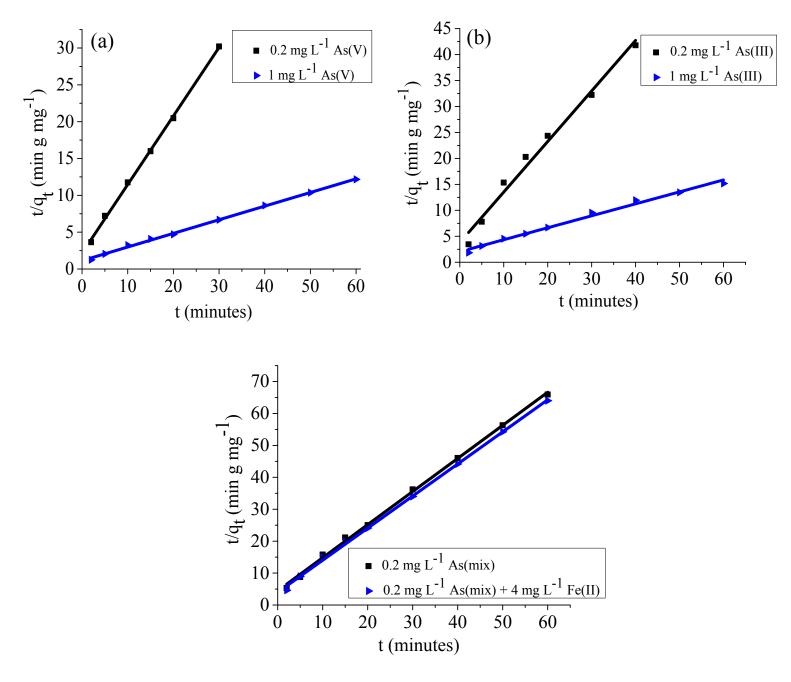


Fig. S2. The pseudo-second order kinetic plots for the adsorption of (a) As(V) (0.2 mg L⁻¹ and 1 mg L⁻¹), (b) As(III)) (0.2 mg L⁻¹ and 1 mg L⁻¹), (c) As(mix)) (0.2 mg L⁻¹) and As(mix) (0.2 mg L⁻¹) in presence of Fe(II) (4 mg L⁻¹) by ZVM. Experimental conditions - adsorbent dose: 0.2 g L⁻¹, volume of solution: 50 mL, pH: 6.5 ± 0.2 and temperature: 298 K.

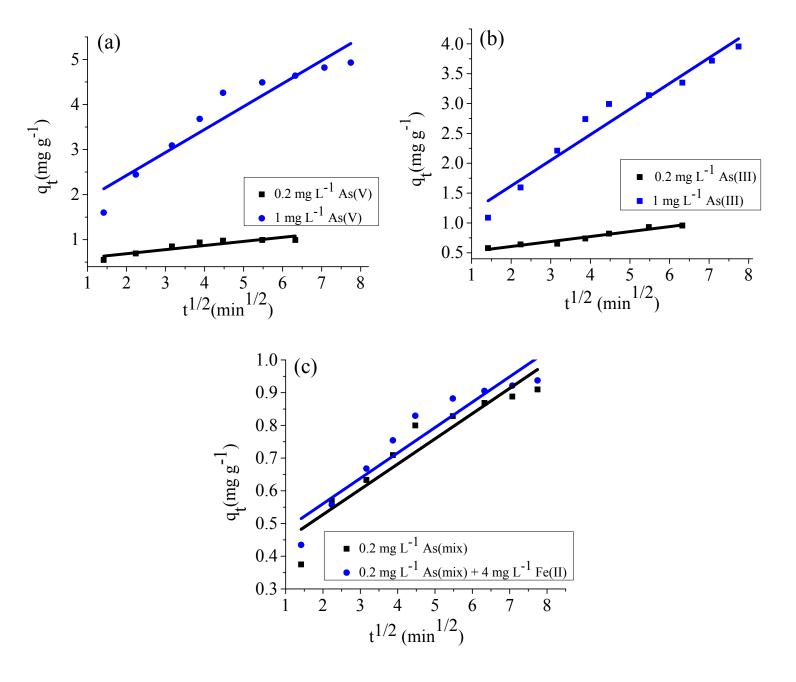


Fig. S3. The intra-particle diffusion kinetic plots for the adsorption of (a) As(V) (0.2 mg L⁻¹ and 1 mg L⁻¹), (b) As(III)) (0.2 mg L⁻¹ and 1 mg L⁻¹), (c) As(mix)) (0.2 mg L⁻¹) and As(mix) (0.2 mg L⁻¹) in presence of Fe(II) (4 mg L⁻¹) by ZVM. Experimental conditions - adsorbent dose: 0.2 g L⁻¹, volume of solution: 50 mL, pH: 6.5 ± 0.2 and temperature: 298 K.

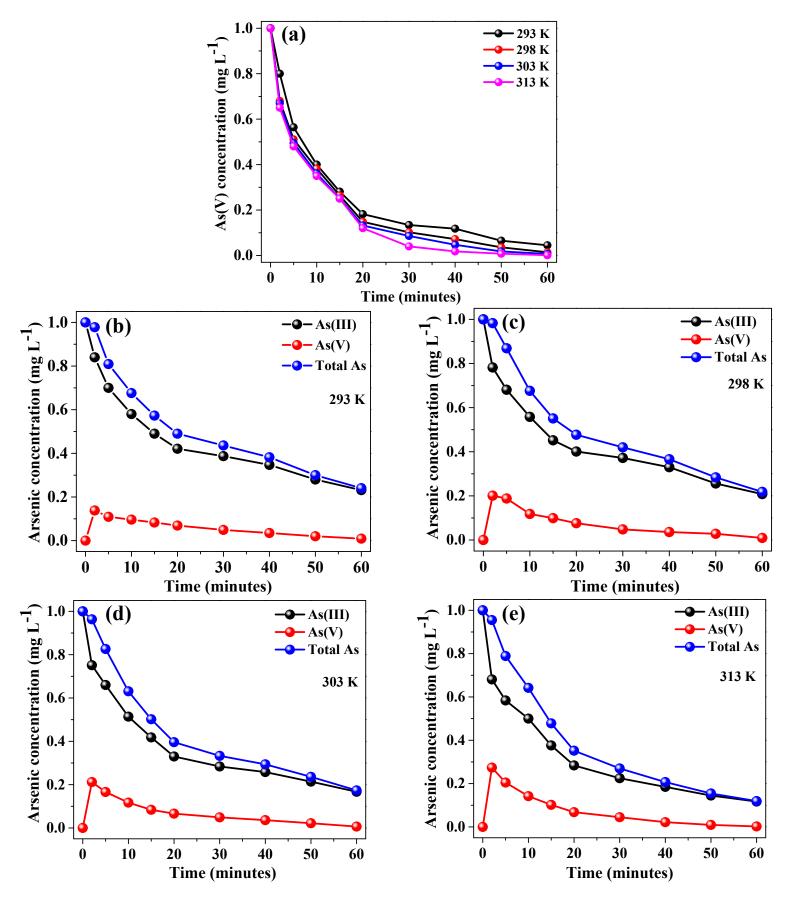


Fig. S4. Kinetics of (a) As(V) and (b-e) As(III) adsorption over ZVM at different temperatures. Experimental conditions: adsorbent dose: 0.2 g L⁻¹, initial conc. of arsenic: 1 mgL⁻¹, volume of solution: 50 mL, pH: 6.5 ± 0.2 .

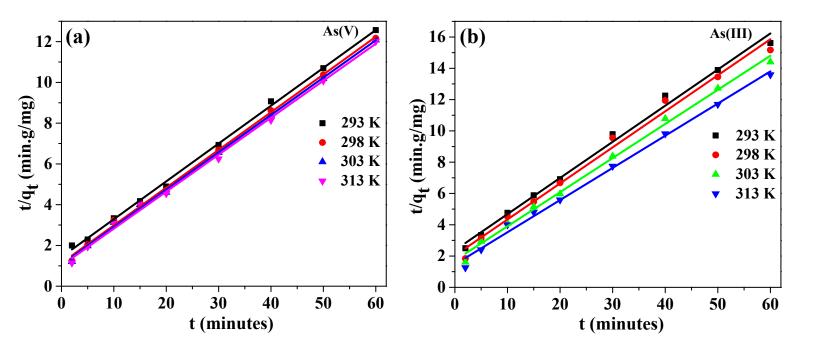


Fig. S5. The pseudo-second order kinetic plots for the adsorption of (a) As(V) and (b) As(III) by ZVM at different temperatures. Experimental conditions - adsorbent dose: 0.2 g L⁻¹, initial conc. of arsenic: 1 mgL⁻¹, volume of solution: 50 mL, pH: 6.5 ± 0.2 .

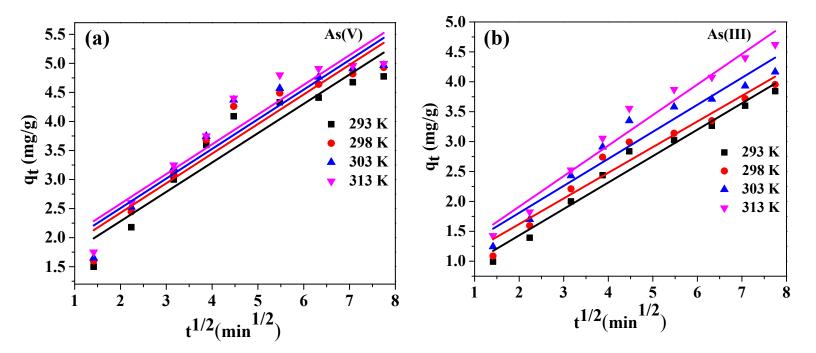


Fig. S6. The intra-particle diffusion kinetic plots for the adsorption of (a) As(V) and (b) As(III) by ZVM at different temperatures. Experimental conditions - adsorbent dose: 0.2 g L⁻¹, initial conc. of arsenic: 1 mgL⁻¹, volume of solution: 50 mL, pH: 6.5 ± 0.2 .

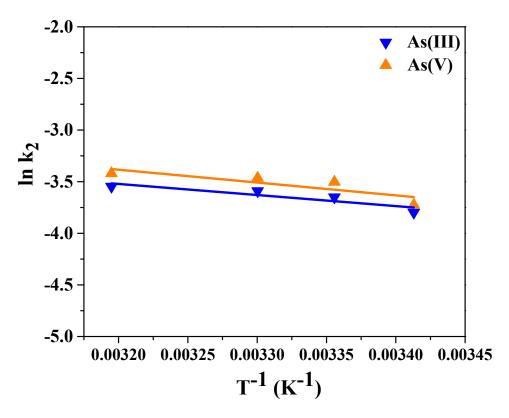


Fig. S7. Arrhenius plots for arsenic sorption on ZVM at different temperatures.

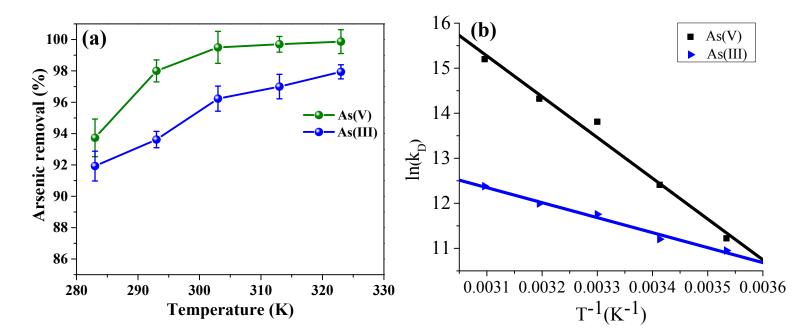


Fig. S8. (a) Effect of temperature on adsorption of As(III) and As(V) by ZVM and (b) The corresponding Van't Hoff plot. Experimental conditions – initial concentration of arsenic: 0.2 mg L⁻¹, adsorbent dose: 0.2 g L⁻¹, volume of solution: 50 mL, contact time: 60 minutes and pH: 6.5 \pm 0.2.

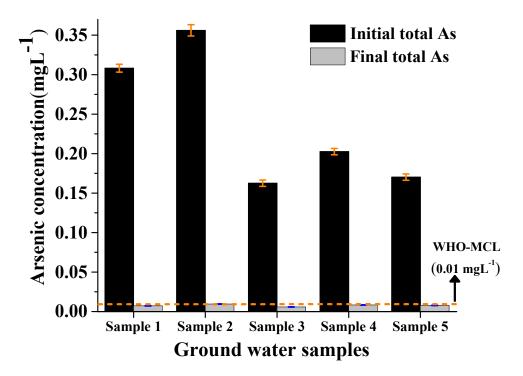


Fig. S9. The arsenic adsorption performance of ZVM with groundwater samples collected form Pathalkudwa Region of Ranchi District, Jharkhand, India. Experimental conditions - adsorbent dose: 0.2 g L⁻¹, volume of solution: 50 mL, contact time: 60 minutes and temperature: 298 K.

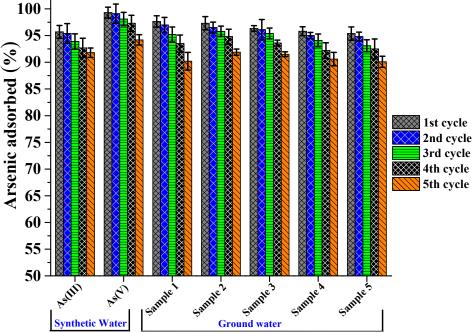


Fig. S10. The reusable efficiency of ZVM with synthetic water and arsenic contaminated ground water after 5 consecutive cycles. Experimental conditions – The initial concentrations of As(III) and As(V): 0.2 mg L⁻¹, adsorbent dose: 0.2 g L⁻¹, volume of solution: 50 mL, contact time: 60 minutes, and temperature: 298 K.

Intra-particle diffusion **Pseudo-first order Pseudo-second order** R² R² С R² $\mathbf{C}_{\mathbf{0}}$ $\mathbf{k_1}$ **k**i \mathbf{k}_2 q_{e(exp)} q_{e(cal)} q_{e(cal)} (mg g-(g mg⁻¹ (mg g ⁻¹ (mg (mg g-(mg g- (\min^{-1}) (mg g⁻ ¹) L-1) 1) min -1/2) 1) 1) \min^{-1}) 0.182 0.400 0.2 0.993 0.741 0.984 1.074 0.998 0.143 0.980 0.367 As(V) 1 4.930 3.450 0.067 0.984 5.400 0.030 0.998 0.509 1.407 0.906 0.090 0.957 0.603 0.887 1.027 0.250 0.985 0.083 0.2 0.439 0.960 As(III) 1 3.955 2.848 0.045 0.955 4.340 0.026 0.990 0.429 0.762 0.953 0.2 0.909 0.510 0.986 0.241 As(mix) 0.063 0.960 0.998 0.077 0.373 0.896 As(mix) 0.2 0.533 0.071 0.994 0.994 0.998 0.905 0.937 0.253 0.0770.405 + Fe(II)

Table S1. The kinetic parameters associated with the adsorptions of different arsenic species of variable concentrations by ZVM.

Table S2. The kinetic parameters associated with the adsorptions of As(III) and As(V) by ZVM at different temperatures.

							Pse	udo-sec	ond				
				Pseudo-first order order				Intra-p					
		Co	q _{e(exp)}	q _{e(cal)}	k ₁	R ²	q _{e(cal)}	k ₂	R ²	ki	С	R ²	. E _a (kJ mol ⁻¹)
		(mg	(mg g-	(mg g-	(\min^{-1})		(mg g-	(g mg-1		(mg g ⁻¹	(mg g-		
		L-1)	1)	1)	()		1)	\min^{-1})		min ^{-1/2})	1)		
	293 K	1	4.775	3.590	0.068	0.964	5.38	0.024	0.998	0.505	1.272	0.872	
As(V)	298 K	1	4.930	3.450	0.067	0.984	5.40	0.030	0.998	0.509	1.407	0.906	- 10.34
115(1)	303 K	1	4.965	3.859	0.080	0.986	5.45	0.031	0.998	0.510	1.483	0.901	
	313 K	1	4.995	4.231	0.096	0.994	5.50	0.032	0.997	0.511	1.559	0.894	-
	293 K	1	3.843	2.918	0.046	0.965	4.32	0.022	0.993	0.415	0.554	0.947	
As(III)	298 K	1	3.955	2.848	0.045	0.955	4.34	0.026	0.990	0.429	0.762	0.953	- 8.91
	303 K	1	4.165	2.87	0.050	0.976	4.58	0.027	0.995	0.451	0.905	0.937	
	313 K	1	4.415	3.218	0.060	0.990	4.86	0.028	0.994	0.455	1.167	0.953	-

	Temperature	ΔG°	ΔH°	ΔS°
	(°C)	(kJ mol ⁻¹)	(kJ mol ⁻¹)	(kJ mol ⁻¹ K ⁻¹)
	10	-26.692		
	20	-30.297		
As(V)	30	-33.902	75.337	0.360
	40	-37.508		
	50	-41.113		
	10	-25.652		
	20	-27.538		
As(III)	30	-29.423	27.708	0.188
	40	-31.309		
	50	-33.194		

Table S3. The thermodynamic parameters associated with the adsorptions of As(V) and As(III) by ZVM.

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
рН	7.13	7.14	6.56	6.94	7.33
Turbidity (NTU)	0.21	0.14	0.01	0.25	0.21
TDS (mg/L)	929	672	683	772	724
Conductivity (µS/cm)	1896	1372	1394	1575	1477
Total Hardness (mg/L)	700	870	660	690	640
Total Alkalinity (mg/L)	150	155	140	145	170
K (mg/L)	13.04	10.47	9.614	8.824	9.39
Ca (mg/L)	209.64	270.52	191.08	196.48	183.2
Mg (mg/L)	46.04	45.88	43.52	47.28	43.64
Na (mg/L)	167.44	166.04	126.56	158.64	117.28
Fe (mg/L)	0.07	0.02	0.03	0.08	0.05
Mn (mg/L)	0.027	0.047	0.257	0.014	0.031
Zn (mg/L)	0.03	0.029	0.05	0.046	0.12
SO ₄ ²⁻ (mg/L)	205.0	160.0	200.0	185.0	120.0
NO ₃ ⁻ (mg/L)	35.0	7.8	3.2	31.0	21.0
Cl⁻(mg/L)	259.15	220.1	216.55	259.15	230.75
PO ₄ ³⁻ (mg/L)	1.15	1.21	1.10	1.32	0.98
HCO ₃ ⁻ (mg/L)	183.0	189.1	170.8	176.9	207.4
F ⁻ (mg/L)	0.23	0.24	0.27	0.25	0.25
As (mg/L)	0.308	0.356	0.162	0.202	0.170

 Table S4. Chemical compositions of collected ground water samples.

				Batch Adsorption	on Studies				
Adsorbent	Experimental Conditions	Effect of pH	Kinetic Studies	Isotherm Studies	Effect of interfering anions	Ground water study	Reuse Studies	– Remarks	Ref.
HBC-Fe ₃ O ₄ - MnO ₂	 Dose: 0.2 g/L pH: 7.0 ± 0.1 Time: 16 hr C₀: 100-800 μg/L As(III/V) Vol. of Sample: 50 ml Temperature: 25° C 	• Maximum removal observed in acidic pH. However removal efficiency decreased with increase of pH and 40% was obtained at pH 9.0.	 97% of removal was achieved in 12 hr for initial concentrations of 100 µg/L As(III)/As(V). Pseudo-second order kinetics 	As(III): q _m = 2.42 mg/g Freundlich isotherm model As(V): q _m = 1.45 mg/g Langmuir isotherm model	 No significant interference of Cl⁻, SO₄²⁻, NO₃⁻. Removal efficiency decreased to 25.49% and 13.80% of As(III) and As(V) in presence of 10mM of PO₄³⁻. 	NR	• The reusability capacity of the material was reduced to 65.5% after 5 th cycle of operation with regeneration of adsorbent.	 Less removal in the neutral pH. Takes extended time of 12 hr to reach equilibrium concentrations Not effective for successive application in treating higher concentration of arsenic contaminated water. Pronounced inhibitory effect of HCO₃⁻ and PO₄³⁻ was witnessed 	51
Aluminium Oxide/Hydroxi de Nanoparticles (AHNP)	 Dose: 2 g/L pH: 7 Time: 300 minutes C₀: 100-1000 μg/L Vol. of Sample: 50 ml Temperature: 25 °C 	 Maximum 85% of removal was observed at pH 7.0 for 500 µg/L of As(III). 	 85% of removal was achieved in 300 minutes for 500 µg/L of arsenic. Pseudo-second order kinetics 	As(III): q _m = 0.833 mg/g Langmuir isotherm model As(V): NR	NR	In groundwater, 8g/L of adsorbent was required to reduce the arsenic concentration (512µg/L) below WHO limit in 300 minutes.	NR	 Takes extended time of 300 minutes to reach equilibrium that too with high amount of adsorbent (2 g/L). The maximum removal efficiency of the material was only 85% for 500g/L Requires higher adsorbent dose to remediate arsenic in groundwater. 	S2
Copper Oxide incorporated mesoporous Alumina (COIMA)	 Dose: 0.4 g/L pH: NR Time: 24 hr C₀: 1 mg/L Vol. of Sample: 50 ml Temperature: 30 ±1 °C 	 Maximum removal observed in acidic pH. At neutral pH the removal of As(V) is around 75% and that of As(III) is around 85%. 	Adsorption equilibrium achieved in 500 minutes.	As(III): q _m = 2.161 mg/g Langmuir isotherm model As(V):): q _m = 2.017 mg/g Langmuir isotherm model	In presence of coexisting anions (PO ₄ ³⁻ , SO ₄ ²⁻ , NO ₃ ⁻ .HCO ₃ ⁻ , CO ₃ ²⁻), As(V) uptake reduced considerably while As(III) removal efficiency decreased to 80% .	NR	Adsorption capacity remains constant after fourth cycles of regeneration and reuse.	 Less effective at neutral pH. Negative effect of coexisting anions in As(V) uptake. Required high reaction time to reach equilibrium. 	\$3

Table S5: Comparison of overall arsenic removal efficiency of ZVM with other adsorbents.

FeOOH/ y- Al ₂ O ₃	 Dose: 5 g/L pH: Natural pH Time: 60 minutes C₀: 10-100 mg/L Vol. of Sample: 220 ml Temperature: 25 °C 	 Maximum removal observed in neutral pH but the final arsenic concentration does not meet the WHO standard. The final pH of the solution reduces to 4.0. 	 Adsorption equilibrium achieved in 60 minutes for initial concentration of 10 mg/L arsenic. Pseudo-second order kinetics. 	As(III): NR As(V):): q _m = 3.541 mg/g Langmuir isotherm model	The presence of SO ₄ ²⁻ , Cl ⁻ and NO ₃ ⁻ had significant negative effects on As(III) adsorption.	NR	NR	•	Requires higher adsorbent dose. The pH of the final solution decreases to 4.0. Final arsenic concentration does not meet the WHO standard.	84
Porous Fe ₃ O ₄ Particles	 Dose: 0.5 g/L pH: 5.0 ± 0.2 Time: 4 hr C₀: 0.1-17 mg/L for As(III) and 0.1-7.5 mg/L for As(V) Vol. of Sample: 10 ml Temperature: 25 °C 	• Adsorption studies conducted at pH 5.0.	 Maximum removal of 90.7% for As(V) and 88.3% for As(III) was achieved in 4 hr for initial concentration of 3 mg/L of As(III) and 3.5 mg/L of As(V). Pseudo-second order kinetics. 	As(III): 6.06 mg/L Freundlich Isotherm As(V):): 6.35 mg/L Langmuir Isotherm	NR	NR	The reusability capacity of the material was reduced to 85% after 5 th cycle of operation with regeneration of adsorbent.		Batch experiments conducted at acidic pH which does not fall under the pH range of drinking water. Shows only 85% of arsenic removal even after regeneration.	85
Fe-MWCNT	 Dose: 1 g/L pH: 4 Time: 1 hr for As(V) and 12 hr for As(III) C₀: 0.1 mg/L Vol. of Sample: 10 ml Temperature:28-40°C 	• Maximum removal for As(V) was observed at pH 4.0 and for As(III) at pH 5.0.	 99 % of As(V) and 80 % of As(III) were removed in 30 minutes for 100 μg/L of arsenic at pH 4.0. Pseudo-second order kinetics. 	As(III): $q_m = 1.723$ mg/gFreundlich isothermmodelAs(V): $q_m = 0.189$ mg/gFreundlich isothermmodel	NR	NR	NR		Batch experiments conducted at pH 4 which does not fall under the pH range of drinking water. Other important adsorption parameters were not studied	86
Copper (II) Oxide	 Dose: 1 g/L pH: 7 Time: 24 hr C₀: 0.5-1 mg/L Vol. of Sample: 100 ml Temperature: 25 ± 2° C 	• 100% arsenic was removed from water at pH above 8.0 while removal percentage decreased to 75% in acidic pH.	 92% removal of As(III) was acheived for initial concentration of 1000 µg/L and 100% removal achieved for 200 µg/L initial arsenic concentration in 3 hr. Pseudo-second order kinetics. 	As(III): q _m = 1.086 mg/g Langmuir isotherm model As(V): NR	 The presence of SO₄²⁻ at very high concentrations (280 mg/L) decreased the arsenic removal percentage by less than 10%. More than 20% decrease in arsenic removal was observed for greater PO₄³⁻ concentrations (0.2 mM). 	NR	• 4% decrease in adsorption efficiency was observed with regenerated adsorbents (for 100 µg/L of arsenic at adsorbent dose of 1 g/L with 3hr of contact time)	• I • I • (Requires extended time of 3 hr to achieve 92% removal for 1 mg/L As(III) concentration. Less selectivity of adsorbent for arsenic in presence of PO_4^{3-} (0.2mM). Adsorption capacity of the adsorbent is very less.	87

FeMn- synergetic adsorbent	 Dose: 2 g/L pH: 3.5 ± 0.1 Time: 24 hr. C₀: 0.45 mg/L Vol. of Sample: NR Temperature: 298 K 	Adsorption studies conducted at 3.5.	 95% removal of As(III) was achieved in 1hr for initial concentration of 0.45 mg/L. Pseudo-second order kinetics 	As(III): q _m = 10.55 mg/g Langmuir isotherm model As(V): NR	• Cl ⁻ , NO ₃ ⁻ and SO ₄ ²⁻ had negligible influence on As(III) removal, while the effect of PO ₄ ³⁻ and SiO ₃ ²⁻ was more pronounced.	NR	• The removal percentages were maintained at nearly 100% during the five cycles with regeneration of adsorbent.	 Batch experiments conducted at pH 3.5 which does not fall under the pH range of drinking water. Requirement of higher adsorbent dose for low arsenic concentration to reach equilibrium. The efficiency of adsorbent was not examined for real groundwater. 	S8
Nanoscale Zero valent iron (NZVI)	 Dose: 1 g/L pH: 7 Time: 12 hr C₀: 1 mg/L of As(III) in 0.01 M NaCl Vol. of Sample: 20 ml Temperature: 25° C 	• 88.6-99.9% removal of As(III) was achieved in pH range 4-10.	 80% of As(III) was removed in 7 minutes for initial concentration of 1 mg/L arsenic. Pseudo-second order kinetics. 	As(III): q _m = 3.5 mg/g Freundlich isotherm model As(V): NR	 No effect of HCO₃⁻, SO₄²⁻ and NO₃⁻. However the presence of 10mM of SiO₄⁴⁻ and PO₄³⁻ reduced As(III) uptake from 99.9 % to 44.94 % and 66.3% 	100% removal efficiency was achieved with 1.0-4.5 g/L of NZVI.	NR	Requirement of greater amount of adsorbent dose for complete removal of As(III) in ground water environment.	<u>\$9</u>
Zero-valent Manganese (ZVM)	 Dose: 0.2 g/L pH: 6.5 ± 0.2 Time: 1 hr. C₀: 0.1-50 mg/L Vol. of Sample: 50 ml Temperature: 25° C 	 More than 90% removal was achieved in a wide pH range (3.0-9.0) for both As(III) and As(V). In neutral pH range, material is capable to reduce the arsenic concentration below WHO limit. 	 Removal of 95.7% and 99.9% was achieved for 0.2 mg/L and 1 mg/L of As(V) in 30 minutes and 1 hr. 99.31% and 89.2% of As(III) was removed for 0.2 mg/L and 1 mg/L of As(III) in 30 minutes and 1 hr. respectively. The presence of Fe(II) enhanced arsenic removal efficiency to 95.24% and 99% in 1 hr compared to the removal achieved in As(mix) solution. Pseudo-second order kinetics 	As(III): q _m = 30.9 mg/g DR isotherm As(V): q _m = 72.5 mg/g DR isotherm	 No major influence of Cl⁻, NO₃⁻, SO₄²⁻. Higher selectivity of ZVM for arsenic over phosphate even at high concentrations.(As:PO₄³⁻ = 1:1,1:5,5:1) 	Arsenic was removed below WHO-MCL limit in all groundwater samples.	Even after 5 th cycle, adsorbent exhibits removal efficiency of 91.8% for As(III) and 94.2% for As(V).	 Provides single step treatment option for total arsenic without any pretreatment. Material exhibits faster kinetics for both As(III) and As(V). Material shows high reuse capacity. Material was efficient enough to remediate total arsenic below the WHO-MCL in ground water environment. 	Our Work

*NR: Not Reported

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