Supplementary Information (SI) for RSC Advances.
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Supplementary Information: MXene-PVA Composite for Arsenic Removal from Industrial Wastewater: A Combined DFT and Experimental Study

Table S1. Computational parameters and convergence tests

Parameter	Value	Convergence criterion
Plane-wave cutoff	500 eV	$\Delta E < 1$ meV/atom
k-point mesh (optimization)	3×3×1	$\Delta E < 5$ meV
k-point mesh (DOS)	5×5×1	-
Force convergence	0.01 eV/Å	-
Energy convergence	10^{-5} eV	-
Vacuum spacing	20 Å	No interaction between images
AIMD time step	1 fs	Energy drift < 1 meV/ps/atom
AIMD cutoff	400 eV	Standard for MD simulations
Dielectric constant (water)	78.4	VASPsol solvation model

Table S2. Bader charge analysis for MXene-PVA-As(V) system

Atom type	Pristine MXene-PVA	With adsorbed As(V)	Charge difference (e^-)
As	-	+1.42	-
O (arsenate)	-	-1.12 (avg)	-
Ti (binding site)	+1.68 (avg)	+1.85 (avg)	+0.17
O (MXene surface)	-1.24 (avg)	-1.38 (avg)	-0.14
O (PVA)	-1.18 (avg)	-1.22 (avg)	-0.04
Total transfer to composite	-	-	0.38

Table S3. Hydrogen bond statistics from AIMD simulations

H-bond type	Average count	Average lifetime (ps)	Distance range (Å)
MXene-OH···O(PVA)	6.2 ± 1.1	3.2 ± 0.8	1.65-1.92
PVA-OH···O(MXene)	2.1 ± 0.7	2.8 ± 0.6	1.70-1.98
As-O···H-O(MXene)	1.4 ± 0.5	4.5 ± 1.2	1.72-1.88
As-O···H-O(PVA)	0.8 ± 0.4	3.9 ± 1.0	1.75-1.95
Water-water	3.8 ± 0.3	1.1 ± 0.3	1.80-2.10

Table S4. XRD peak assignments for Ti_3AlC_2, MXene, and MXene-PVA

Material	2θ (°)	d-spacing (Å)	Miller indices	Assignment
Ti_3AlC_2	9.5	9.3	(002)	MAX phase basal plane
	19.1	4.6	(004)	MAX phase
	34.2	2.6	(101)	MAX phase
	39.0	2.3	(103)	MAX phase
	41.8	2.2	(104)	MAX phase

Material	2θ (°)	d-spacing (Å)	Miller indices	Assignment
	60.2	1.5	(110)	MAX phase
$Ti_3C_2T_x$	6.2	14.2	(002)	Expanded MXene interlayer
	18.4	4.8	(004)	MXene second order
	27.8	3.2	(006)	MXene third order
	60.5	1.5	(110)	In-plane Ti-C
MXene-PVA	5.4	16.3	(002)	PVA-intercalated MXene
	19.5	4.5	-	Semi-crystalline PVA
	27.2	3.3	(006)	MXene higher order

Table S5. FTIR peak assignments and intensities

Wavenumber (cm^{-1})	Assignment	Pristine MXene	MXene-PVA	As-loaded MXene-PVA
3440	O-H stretching	Strong, broad	-	-
3385	O-H stretching (H-bonded)	-	Strong, broad	-
3420	O-H stretching (modified)	-	-	Medium, narrow
2920	C-H asymmetric stretch	-	Medium	Medium
2850	C-H symmetric stretch	-	Medium	Medium
1627	Ti-OH bending	Medium	-	-
1618	Ti-OH bending (shifted)	-	Weak	Very weak
1430	C-H bending (PVA)	-	Medium	Medium
1402	C-O stretching	Weak	Weak	Weak
1090	C-O stretching (PVA)	-	Strong	Strong
825	As-O stretching	-	-	Strong
593	Ti-O vibration	Strong	Strong	-
601	Ti-O vibration (perturbed)	-	-	Strong, broad

Table S6. N_2 adsorption-desorption isotherm analysis

Parameter	Pristine MXene	MXene-PVA	Method
BET surface area (m^2/g)	32.5 ± 1.2	56.8 ± 2.1	Multi-point BET
Langmuir surface area (m^2/g)	44.7	78.3	Langmuir equation
Total pore volume (cm^3/g)	0.18	0.31	$P/P_0 = 0.99$
Micropore volume (cm^3/g)	0.02	0.04	t-plot method
Mesopore volume (cm^3/g)	0.14	0.24	BJH desorption
Average pore diameter (nm)	3.8	8.5	4V/A by BET
BJH adsorption pore size (nm)	4.2	9.1	BJH method
BJH desorption pore size (nm)	3.8	8.5	BJH method

Table S7. TGA-DTG analysis details

Material	Temperature range (°C)	Weight loss (%)	DTG peak (°C)	Assignment
MXene	30-200	5.2	85	Adsorbed water
	200-400	4.8	285	-OH, -F desorption
	400-600	3.3	495	Partial oxidation
	600-800	+12.3	-	Oxidation to TiO_2
MXene-PVA	30-150	7.8	75	Water evaporation
	150-250	18.5	210	PVA dehydration
	250-350	24.7	305	PVA chain scission
	350-450	15.0	385	PVA carbonization
	450-600	9.4	520	Complete degradation
	600-800	Gradual	-	MXene oxidation

Table S8. XPS detailed peak fitting parameters

Element	Peak	BE (eV)	FWHM (eV)	Area (%)	Assignment
Pristine MXene-PVA					
Ti $2p_{3/2}$	1	454.8	0.9	46.1	Ti-C
	2	455.8	1.1	32.8	Ti^{2+}
	3	457.1	1.3	18.6	Ti^{3+}
	4	458.9	1.5	2.5	Ti^{4+} (TiO_2)
O 1s	1	529.8	1.2	18.4	C-Ti-O_x
	2	531.2	1.5	45.8	Ti-OH
	3	532.3	1.4	28.6	C-O (PVA)
	4	533.5	1.6	7.2	H_2O
As-loaded MXene-PVA					
As 3d	$3d_{5/2}$	44.8	1.1	61.2	As(V)-O
	$3d_{3/2}$	45.5	1.1	38.8	As(V)-O
Ti $2p_{3/2}$	1	454.8	0.9	44.8	Ti-C
	2	455.9	1.2	30.5	Ti^{2+}
	3	457.2	1.3	17.2	Ti^{3+}
	4	459.3	1.6	7.5	Ti^{4+}
O 1s	1	529.8	1.2	15.8	C-Ti-O_x
	2	530.4	1.3	8.2	As-O-Ti
	3	531.4	1.6	38.5	Ti-OH (H-bonded)
	4	532.3	1.4	30.8	C-O (PVA)
	5	533.5	1.6	6.7	H_2O

Table S9. Comparison of kinetic models

Model	Equation	Parameters	R^2	χ^2	RMSE
Pseudo-first-order	$\ln(q_e-q_t) = \ln(q_e) - k_1 t$	q_e = 78.2 mg/g; k_1 = 0.0082	0.921	15.8	8.4

Model	Equation	Parameters	R^2	χ^2	RMSE
Pseudo-second-order	$t/q_t = 1/(k_2 q_e^2) + t/q_e$	q_e = 96.1 mg/g; k_2 = 0.0061 g/mg·min	0.994	1.2	2.1
Elovich	$q_t = (1/\beta)\ln(\alpha\beta) + (1/\beta)\ln(t)$	α = 18.5 mg/g·min; β = 0.052 g/mg	0.968	6.3	4.5
Intraparticle diffusion	$q_t = k_{int}t^{0.5} + C$	k_{int} = 4.82 mg/g·min^0.5; C = 32.1	0.945*	-	-

*Multi-linear fit with three stages

Table S10. Temperature-dependent rate constants and activation energy

Temperature (°C)	k_2 (g/mg·min)	ln(k_2)	1000/T (K^{-1})	E_a (kJ/mol)	A (g/mg·min)
15	0.0042	-5.473	3.472		
25	0.0061	-5.100	3.356	23.7	1.82×10^3
35	0.0084	-4.780	3.247		
45	0.0115	-4.465	3.145		

Activation energy calculated from Arrhenius plot: ln(k_2) vs. 1/T, slope = $-E_a/R$

Table S11. Isotherm model parameters at different temperatures

T (°C)	Langmuir Model			Freundlich Model		
	q_{max} (mg/g)	K_l (L/mg)	R^2	Kf	n	R^2
15	122.8	0.132	0.989	24.8	2.71	0.948
25	135.2	0.148	0.992	28.4	2.83	0.951
35	142.6	0.161	0.994	31.2	2.92	0.946
45	148.9	0.175	0.991	33.8	3.01	0.943

Table S12. Thermodynamic parameters calculation

T (K)	Kd (L/g)	ln(Kd)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol·K)
288	276.8	5.623	-2.8		
298	310.4	5.738	-3.5	+18.3	+68.5
308	347.2	5.850	-4.1		
318	388.5	5.962	-4.8		

Van't Hoff equation: $\ln(Kd) = \Delta S°/R - \Delta H°/RT$; $\Delta G° = \Delta H° - T\Delta S°$

Table S13. Effect of initial pH on zeta potential and surface speciation

pH	Zeta potential (mV)	Dominant As(V) species	Dominant As(III) species	Surface charge

pH	Zeta potential (mV)	Dominant As(V) species	Dominant As(III) species	Surface charge
3	-12.4 ± 1.8	$H_2AsO_4^-$ (92%), H_3AsO_4 (8%)	H_3AsO_3 (100%)	Slightly negative
5	-23.8 ± 2.1	$H_2AsO_4^-$ (96%), $HAsO_4^{2-}$ (4%)	H_3AsO_3 (100%)	Negative
7	-31.5 ± 1.9	$H_2AsO_4^-$ (78%), $HAsO_4^{2-}$ (22%)	H_3AsO_3 (98%), $H_2AsO_3^-$ (2%)	Negative
9	-38.9 ± 2.4	$HAsO_4^{2-}$ (88%), $H_2AsO_4^-$ (12%)	$H_2AsO_3^-$ (65%), H_3AsO_3 (35%)	Highly negative
11	-42.7 ± 2.2	$HAsO_4^{2-}$ (52%), AsO_4^{3-} (48%)	$H_2AsO_3^-$ (95%), $HAsO_3^{2-}$ (5%)	Highly negative

Table S14. Selectivity coefficients (α) for various competing ions

Competing ion	Concentration ratio (ion:As)	Kd,As (mL/g)	Kd,ion (mL/g)	α (As/ion)	Interference level
PO_4^{3-}	1:1	2163	774	2.8	High
PO_4^{3-}	5:1	1082	425	2.5	Very high
PO_4^{3-}	10:1	713	298	2.4	Severe
SO_4^{2-}	10:1	2240	185	12.1	Low
HCO_3^-	15:1	2485	142	17.5	Very low
NO_3^-	10:1	2615	95	27.5	Minimal
Cl^-	28:1	2667	82	32.5	Negligible
F^-	5:1	2420	312	7.8	Low

Table S15. Column study parameters and performance

Parameter	Value	Unit
Column diameter	2.5	cm
Bed height	15.0	cm
Bed volume	73.6	mL
Adsorbent mass	18.5	g
Bulk density	0.251	g/cm³
Bed porosity	0.68	-
Flow rate	5.0	mL/min
Linear velocity	1.02	cm/min
EBCT	9.2	min
Hydraulic loading rate	2.45	m/h

Parameter	Value	Unit
Influent As concentration	8.2	mg/L
Breakthrough point (C/C_0=0.05)	148	BV
Saturation point (C/C_0=0.95)	412	BV
Total volume treated (breakthrough)	10.9	L
Dynamic adsorption capacity	142.3	mg/g
Utilization efficiency	84.5	%
Thomas rate constant (KT_h)	0.0142	mL/min·mg
Thomas capacity (q_0)	145.7	mg/g

Table S16. Real wastewater detailed composition

Parameter	Electroplating wastewater	Mining wastewater	Unit	Method
pH	6.8 ± 0.1	5.2 ± 0.2	-	pH meter
Conductivity	3850 ± 120	5620 ± 180	μS/cm	Conductivity meter
TDS	2340 ± 85	3890 ± 145	mg/L	Gravimetric
Total As	8.2 ± 0.3	15.7 ± 0.6	mg/L	ICP-OES
As(V)	7.6 ± 0.3	14.0 ± 0.5	mg/L	HPLC-ICP-MS
As(III)	0.6 ± 0.1	1.7 ± 0.2	mg/L	HPLC-ICP-MS
SO_4^{2-}	485 ± 18	1240 ± 52	mg/L	IC
PO_4^{3-}	12.3 ± 0.8	3.8 ± 0.4	mg/L	IC
Cl^-	820 ± 35	340 ± 18	mg/L	IC
NO_3^-	15.8 ± 1.2	8.4 ± 0.9	mg/L	IC
Ca^{2+}	125 ± 8	88 ± 6	mg/L	ICP-OES
Mg^{2+}	45 ± 4	32 ± 3	mg/L	ICP-OES
Fe	2.4 ± 0.2	34.2 ± 2.1	mg/L	ICP-OES
Mn	0.8 ± 0.1	18.6 ± 1.2	mg/L	ICP-OES
Cu	8.5 ± 0.5	1.2 ± 0.2	mg/L	ICP-OES
Ni	3.2 ± 0.3	0.4 ± 0.1	mg/L	ICP-OES
Zn	5.8 ± 0.4	2.1 ± 0.3	mg/L	ICP-OES
Pb	0.18 ± 0.03	0.08 ± 0.02	mg/L	ICP-MS
Cd	0.04 ± 0.01	0.02 ± 0.01	mg/L	ICP-MS
Cr(total)	1.2 ± 0.2	0.3 ± 0.1	mg/L	ICP-OES
TOC	45.2 ± 3.2	28.7 ± 2.5	mg/L	TOC analyzer
COD	152 ± 12	98 ± 9	mg/L	Dichromate method
Alkalinity (as $CaCO_3$)	185 ± 15	45 ± 8	mg/L	Titration

Table S17. Economic analysis for 8-cycle regeneration

Cost parameter	Single-use	8-cycle reuse	Unit	Savings (%)
Adsorbent cost	15.50	1.94	$/kg treated water	87.5
NaOH (regeneration)	0	0.85	$/kg treated water	-

Cost parameter	Single-use	8-cycle reuse	Unit	Savings (%)
Water (washing)	0	0.22	$/kg treated water	-
Energy (drying)	0	0.48	$/kg treated water	-
Labor	2.00	2.80	$/kg treated water	-40.0
Total operational cost	17.50	6.29	$/kg treated water	64.1
Volume treated per kg adsorbent	62.5	187.5	L/kg	+200
Cost per m³ wastewater	280	92	$/m³	67.1

Assumptions: Adsorbent cost $45/kg; NaOH $0.50/kg; electricity $0.15/kWh; labor $20/h