Electronic Supplementary Information

A report on arsenic removal from water via adsorption of arsenomolybdate complex on S−$CuFe_2O_4$ adsorbents†

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Section I

List of Abbreviations

AMC = Arsenomolybdate complex

Emu/g = Electromagnetic unit

As^{+3} = Arsenic (III)

As^{+5} = Arsenic (IV)

K_L = Langmuir model

K_F = Freundlich model

K_T = Temkin model

K_d = Intra-particle diffusion

K_1 = Pseudo-first order reaction

K_2 = Pseudo-second order reaction

LA = Layyah

Conformation through arsenic Quick ™ kit:

The reaction bottles were filled with the water sample (treated with adsorbent) up to the marked line. The first chemical labeled as level 3 pink teaspoons (in the kit box) was then added to reaction bottles. The reaction bottles were then tightly closed and shaken for 10 seconds to allow the material to settle down to overcome the sulfide interference**.** Then, the reaction bottles were filled with three level white teaspoons of chemical no.3 zinc mesh and were sealed tightly and vigorously shaken for approximately five seconds. After then, the arsenic test strip was precisely fitted into the turret, so that the red line imprinted on the strip was placed behind the reaction bottles. The yellow cape has been removed and replaced with a white cap that contains an arsenic testing strip inside. During the experiment stopwatch was used to monitor the changes during the process. The reaction was completed in around ten minutes and the white strip was carefully removed and the color that appeared matched exactly with the Quick™ Easy Read ™ color chart. In order to identify the treated solution and to measure the quantity of the residual arsenic, a test strip and a standard chart from an arsenic kit was used. The results were then observed and recorded carefully.

Section II

Chemical equation for AMC:

$$Na_2HAsO_4.7H_2O + (NH_4)MoO_4 + C_8H_4K_2O_{12}Sb_2 + C_6H_8O_6 + H_2SO_4$$

$$\downarrow$$

$$Na_3[As_3Mo_2O_{15}].10H_2O \text{ (AMC)}$$

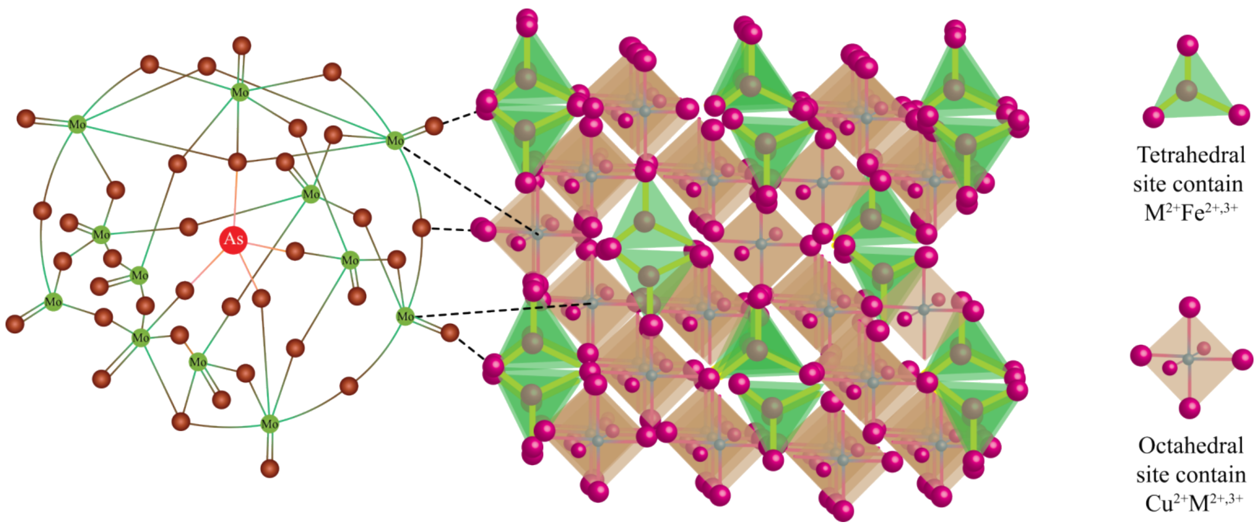

Figure S1: Structure of arsenomolybdate blue complex adsorbed on $CuFe_2O_4$.

Table S1: The adsorption parameters used during the removal of arsenic from solution

Parameters to be optimized	**Fixed parameters**					**Variables parameters**	**Optimum**
	Temp (°C)	**Contact time(min)**	**pH**	**Adsorbent dose (mg)**	**Initial Arsenic concentration (mg/L)**		
Solution pH	25	30	----	50	10	3 to 9	6.5
Temperature (°C)	----	30	6.5	50	10	20−60 °C	35 °C
Contact time (min)	35	----	6.5	50	10	1−30 min	20 min
Concentration (mg/L)	35	20	6.5	50	---	1−20 ppm	10 ppm
Adsorption dose (mg)	35	20	6.5	---	10	10−70 mg	55 mg

Section III

λ−max Determination of Arsenomolybdate Blue complex:

Ultraviolet (UV) spectrophotometer was initially switched on, then after five minutes, a wavelength of 400 nm was set as the initial wavelength. Distilled water was then used for calibrating the instrument. Sample solution was then placed in a UV spectrophotometer, and initial wavelength was calculated. The absorbance has been determined by maintaining a difference of 10 nm at regular intervals. The absorbance started to rise until it reached a certain limit, at which it began to drop. Lambda max (λ) values for the 10 ppm solution were obtained by plotting a graph of absorbance (A) against time (t), which was obtained from all absorbance measurements completed up to this point at regular intervals. Because of the different concentration ofAs^{+5} in the solution, the process was applied to each sample which included the untreated complex, and the absorbance value fluctuated throughout the process. Maximum absorbance value measured at 850 nm is about 0.825. Figure.6 (b) represents the λ−max of AMC.

Table S2: Kinetic parameters: Pseudo-first order, pseudo-second-order, Liquid film diffusion model and intra-particle diffusion model, Isotherm parameters for the Langmuir, Freundlich and Temkin model.

Kinetic models	Parameters		
Pseudo−first order	$K_1 = 6.5 \times 10^{-3}$	q_e (mg/g) = 1.2893	R^2=0.76418
Pseudo−Second order	$K_2\left(\frac{g}{mg}\right) = 2.294 \times 10^{-5}$	q_e (mg/g) = 180.83	$R^2 = 0.99997$
Intra−Particle diffusion	K_d $(mg/gh) = 90.905$	----	$R^2 = 0.69763$
Liquid-film diffusion	$K_F = 1.0243$	-----	$R^2 = 0.65103$
Langmuir	$K_L\left(\frac{L}{mg}\right) = 0.000311$	$q_{max} = 381.679$	$R^2 = 0.97021$
Freundlich	$K_F\left(\frac{mg}{g}\right) = 512.125$	$1/n = 0.2218$	$R^2 = 0.9058$
Temkin(mg/gh$^{-0.5}$)	$K_T\left(\frac{L}{mg}\right) = 5606.76$	-----	$R^2 = 0.87431$

Table S3: EDX analysis weight and amount percentage of element in as−synthesized adsorbent S−$CuFe_2O_4$.

Elements	Wt.%	At. %
S	2.51	2.63
O	25.8	54.6
C	0.60	1.68
Cu	24.2	12.38
Fe	46.8	28.26
Total	100	100

Table S4: Comparison of Freundlich, Langmuir and Temkin models parameters with reported adsorbent.

Sr.No	Adsorbent	K_F ($L.mg^{-1}$)	K_L ($mg.g^{-1}$)	K_T ($L.mg^{-1}$)	Ref.
1	GNPs/$CuFe_2O_4$	10.31	0.02	---	[1]
2	Pb(II)/$NiFe_2O_4$	48.8	0.1878	1.19	[2]
3	As(V)/$0.8Ni_{0.5}Zn_{0.5}Fe_2O_4/0.2SiO_2$	98.3787	114.6789	5.5601	[3]
4	Porous copper ferrite foam	29.28	0.32	----	[4]
5	Graphene oxide/$CuFe_2O_4$ foam	16.49	0.046	----	[5]
6	Cobalt ferrite nanoparticles	175.56	----	-----	[6]
7	S-$CuFe_2O_4$	512.125	0.000311	5606.76	This work

Table S5: Comparison for adsorption capacities of $CuFe_2O_4$ and S-$CuFe_2O_4$.

Adsorbent	pH	Adsorption capacity of As^{3+} (mg/g)	Adsorption capacity of As^{5+} (mg/g)	Ref.
$CuFe_2O_4$ binary oxide	7	122.3	82.7	[7]
GNPs/Fe-Mg oxide	7	103.9	103.9	[1]
$FeMn_x$/RGO	7	13.1	5.83	[8]
$Mg_{0.27}Fe_{2.5}O_4$	5.2	127.4	83.2	[9]
Fe_2O_4/MnO_2	6.2	2.89	3.84	[10]
$MnFe_2O_4$ NCs	---	27.27	-----	[11]
$CuFe_2O_4$ (Powder)	7.3	41.2	------	[12]
$CuFe_2O_4$ (Foam)	6.5	44.0	85.4	[5]
$MnFe_2O_4$ (Powder)	7.5	94	90	[13]
$CuFe_2O_4$	6.5	140.21	140.21	This work
S-$CuFe_2O_4$	6.5	181.81	181.81	This work

Table S6: Parameters of VSM.

Adsorbent	H_c (Oe)	M_s (emu g^{-1})	M_r (emu g^{-1})	S (M_r/M_s)
$CuFe_2O_4$	191.51	60.8	12.30	0.2023
S−$CuFe_2O_4$	314.63	69.35	15.91	0.2294

Section IV

Sampling from field:

For the purpose of estimating and eliminating the total arsenic, 50water samples from various areas of District Layyah were collected. According to the survey, water obtained from hand pumps has slightly higher concentration of arsenic contents as compared to water collected from other sources such as tube well, motors etc. The average arsenic concentration in ground drinking water of District Layyah measured was 176.38 ppb (i.e. higher the limit set by World Health Organization recommendations). The survey results indicated that the community having high levels of arsenic in drinking water have been affected from various arsenical disorders. The arsenic level in ground drinking water of the affected areas was carefully examined by our team members. To remove arsenic from contaminated water, 1g of synthesized $S{-}CuFe_2O_4$ adsorbent was used under nominal conditions. In District Layyah, where the average level of arsenic in water was 176.38 ppb, 1 g of as−synthesized adsorbent can give up to 272.4 gals of arsenic free−water. The maximum adsorption capacity of the aforementioned adsorbent measured was 181.81mg/g.

Section V

Protonation of AMC:

$$AMC^{3-} + H^{+} \rightarrow HAMC^{2-} \quad (1)$$

$$AMC^{3-} + 2H \rightarrow H_2AMC_4^{-} \quad (2)$$

$$AMC_4^{3-} + 3H \rightarrow H_3AMC_4^{-} \quad (3)$$

Arsenate (AMC) absorption:

$$M + AMC^{3-} + 2H^{+} \rightarrow MH_2AMC \quad (4)$$

$$M + AMC^{3-} + H^{+} \rightarrow MHAMC^{-} \quad (5)$$

$$M + AMC^{3-} + H^{+} \rightarrow MAsO_4^{2-} \quad (6)$$

Table S7: Arsenic elimination from the ground drinking water of District Layyah using 1 g of S−$CuFe_2O_4$ adsorbent

Sample Code	Location	Source	Source depth	As in (ppb)	Abs* AMC	Abs** AMC	As Quick™ Tests	GPS (Meterk/Handheld-ZL-180)		
								E°	N	Ele.
LA-1	Kharal azeem	Hand pump	80	250	0.160	0.000	0	70°56’23.6720	30°57’53.1000	147m
LA-2	Khan wala	Tube well	200	100	0.070	0.000	0	70°56’23.6630	30°57’53.800	125
LA-3	Hafiz abad	Motor pump	160	110	0.090	0.000	0	70°56’23.6690	30°57’53.830	122
LA-4	Shah jamal	Hand pump	95	280	0.170	0.000	0	70°56’23.6698	30°57’53.840	133
LA-5	Jaman shah	Hand pump	90	200	0.140	0.000	0	70°56’23.6710	30°57’53.855	124
LA-6	Jaisal	Motor pump	150	160	0.130	0.000	0	70°56’23.6730	30°57’53.850	135
LA-7	Shah sultan	Hand pump	60	180	0.120	0.000	0	70°56’23.6750	30°57’53.855	126
LA-8	Wanjhery wala	Hand pump	70	300	0.180	0.000	0	70°56’23.6780	30°57’53.860	137
LA-9	Hazar shah wala	Motor pump	150	130	0.090	0.000	0	70°56’23.6790	30°57’53.865	142
LA-10	Dasti wala	Hand pump	80	190	0.150	0.000	0	70°56’23.6795	30°57’53.870	133
LA-11	Basti malwana	Hand pump	75	240	0.145	0.000	0	70°56’23.6830	30°57’53.875	127
LA-12	Noor abad	Tube well	300	150	0.135	0.002	0-3	70°56’23.6850	30°57’53.880	135
LA-13	Mohalla arifabad	Hand pump	60	100	0.070	0.000	0	70°56’23.6870	30°57’53.889	136
LA-14	Faqirwala	Tube well	350	105	0.060	0.003	0-4	70°56’23.6890	30°57’53.890	127
LA-15	Noon wala	Hand pump	70	120	0.101	0.000	0	70°56’23.6940	30°57’53.895	115
LA-16	Mohalla faizabad	Hand pump	90	110	0.650	0.000	0	70°56’23.6950	30°57’53.900	120
LA-17	Basti machi	Tube well	350	80	0.050	0.003	0-4	70°56’23.6960	30°57’53.910	127
LA-18	Paki sagwan wali	Hand pump	60	190	0.135	0.000	0	70°56’23.6970	30°57’53.925	119
LA-19	Basti wasava shumali	Tube well	200	80	0.050	0.000	0	70°56’23.6980	30°57’53.930	120
LA-20	Basti sawan wala	Hand pump	80	145	0.0135	0.000	0	70°56’23.6990	30°57’53.935	133

LA-21	Dajal wala	Tubewell	200	140	0.350	0.000	0	70°56’23.6995	30°57’53.940	131
LA-22	Mohalla bilal nagger	Tube well	280	150	0.505	0.001	0-2	70°56’23.6999	30°57’53.945	125
LA-23	Marnay shah	Hand pump	80	100	0.070	0.000	0	70°56’23.6998	30°57’53.950	129
LA-24	Tibbi Maharan	Tube well	300	130	0.130	0.000	0	70°56’23.7156	30°57’53.955	130
LA-25	Litti wala	Hand pump	80	180	0.160	0.000	0	70°56’23.7169	30°57’53.955	128
LA-26	Basti Deen pur	Hand pump	90	250	0.170	0.000	0	70°56’23.7173	30°57’53.956	130
LA-27	Mahi wala	Tube well	300	140	0.131	0.000	0	70°56’23.7174	30°57’53.960	132
LA-28	Gujie kot sultan	Tube well	200	110	0.070	0.000	0	70°56’23.7176	30°57’53.965	134
LA-29	Riaz abad	Hand pump	95	180	0.160	0.000	0	70°56’23.7179	30°57’53.970	144
LA-30	Norang wala	Hand pump	75	200	0.140	0.000	0	70°56’23.7135	30°57’53.975	110
LA-31	Mangla	Hand pump	80	280	0.170	0.001	0-2	70°56’23.7138	30°57’53.980	115
LA-32	Shahadat wala	Tube well	200	180	0.160	0.000	0	70°56’23.7139	30°57’53.985	124
LA-33	Yousaf wala	Hand pump	60	300	0.190	0.002	0-3	70°56’23.7235	30°57’53.990	135
LA-34	Rehman abad	Tube well	160	105	0.060	0.000	0	70°56’23.7236	30°57’53.940	138
LA-35	Basti shah nawaz	Hand pump	50	170	0.120	0.000	0	70°56’23.7245	30°57’53.899	137
LA-36	Tahli wala	Hand pump	75	280	0.170	0.001	0-2	70°56’23.7255	30°57’53.934	144
LA-37	Indus river	River	----	210		0.000	0	70°56’23.7256	30°57’53.980	135
LA-38	Mochi wala	Hand pump	60	300	0.190	0.002	0-3	70°56’23.7258	30°57’53.910	129
LA-39	Bypass	Motor pump	110	190	0.1850	0.000	0	70°56’23.7259	30°57’53.888	138
LA-40	Chandran	Hand pump	70	200	0.140	0.000	0	70°56’23.7266	30°57’53.899	139
LA-41	Layyah minor	Motor pump	105	180	0.160	0.000	0	70°56’23.7277	30°57’53.850	130
LA-42	Railway	Hand pump	65	200	0.140	0.000	0	70°56’23.7379	30°57’53.890	142
LA-43	THQ kot sultan	Motor pump	130	80	0.050	0.000	0	70°56’23.7480	30°57’53.870	141
LA-44	Pull Angra Road	Canal	------	180		0.000	0	70°56’23.7499	30°57’53.976	143
LA-45	Basti arain	Hand pump	80	170	0.140	0.000	0	70°56’23.7550	30°57’53.889	145

LA-46	Phar pur	Hand pump	70	160	0.120	0.000	0	70°56’23.7570	30°57’53.990	140
LA-47	Mohalla mohsin abad	Motor pump	120	200	0.140	0.000	0	70°56’23.7589	30°57’53.988	139
LA-48	Layyah minor	Hand pump	60	300	0.190	0.002	0-3	70°56’23.7599	30°57’53.1000	137
LA-49	Ada ijaz abad	Hand pump	80	280	0.170	0.001	0-2	70°56’23.7619	30°57’53.999	147
LA-50	Thal chowk/bail chowk	Hand pump	70	260	0.150	0.000	0	70°56’23.7624	30°57’53.990	143

Table S8: Survey results and reports obtained from District Layyah (Punjab. Pakistan)

Survey month	Samples*		Survey location				
			Kot sultan	Hafiz abad	Shah jamal	Jaman shah	Kharal azeem
September	25	Max As (ppb)	260	200	380	290	400
		Min As (ppb)	130	80	140	160	170
		Average	195	140	260	225	285
October	15	Max As (ppb)	350	290	190	350	250
		Min As (ppb)	150	120	50	150	130
		Average	250	205	120	250	190
November	10	Max As (ppb)	370	400	300	290	190
		Min As (ppb)	180	180	120	160	80
		Average	275	290	210	225	135

Table S9: Team members involved in survey and project

Sr. No.	Name of Survey Team	Designation/Responsibilities
1	Dr. Ejaz Hussain	Project administration/supervision
2	Meryam Sultana	Research student, Sampling/field assistant
3	Muhammad Zeeshan Abid	Research student, Results Interpretation
4	Aqsa Khan Buzdar	Research student/Field Assistant
5	Muhammad Jalil	Research student/Driver
6	Prof. Dr. Abdul Rauf	Instrumental access
7	Dr. Khezina Rafiq	Field coordinator/administrator

Table S10: Persons that were hired from areas of survey.

Sr. No.	Name of Volunteers	Volunteer participation/services
1	Muhammad Zeeshan	Contributed as local guide/translator for public counseling in native languages
2	Muhammad Arbaz	Volunteer serve tea and breakfast
3	Farhan Ali	Volunteer serve as jockey person/entertainment/songs for survey team
4	Sobia Ramzan	She voluntarily serves with traditional lassi

Note: All authors thanks and acknowledges the volunteers services. Services of these members were voluntarily contributed on the basis of their own wishes’

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