Supporting Information

Tunable Sulphur Doping in $CuFe_2O_4$ for Efficient Removal of Arsenic through Arsenomolybdate Complex Adsorption: Kinetics, Isothermal and Mechanistic Studies

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Section 1

Confirmation through arsenic Quick™ kit: The sample of water (treated water with adsorbent) was taken and added in the reaction bottle up to marked line. The first chemical, level 3 pink spoonfuls (present in kit box), was then added to the reactions bottles. The reaction bottles were then tightly sealed and vigorously shaken for 10 seconds, allowing the sample to settle to overcome sulfide interference. After that 3 level white spoonful of chemical no 3 zinc mesh was added into the reaction bottle and then capped tightly and shacked violently about 5 seconds. Then the arsenic test strip that is fitted into the turret such precisely that the red line which was imprinted on the strip was putted behind the reaction bottle. A new, white-colored cap that contains an arsenic testing strip was inserted after the yellow cape was removed. Stopwatch must be used during the experiments. Then after the reaction had finished, which took around 10 minutes, the white strip was carefully removed, and the color was produced matched with the Quick ™ Easy Read ™ color chart. So, using a test strip and a standard chart from an arsenic kit, we were able to identify the treated solution and determine the amount of arsenic which is left over. The results were then noted and recorded [1].

Section 2

Chemical equation:

$Na_2HAsO_4.7H_2O + (NH_4)\ MoO_4 + C_8H_4K_2O_{12}Sb_2 + C_6H_8O_6 + H_2SO_4 \rightarrow Na_3[As_3MoO_{15}].10H_2O$

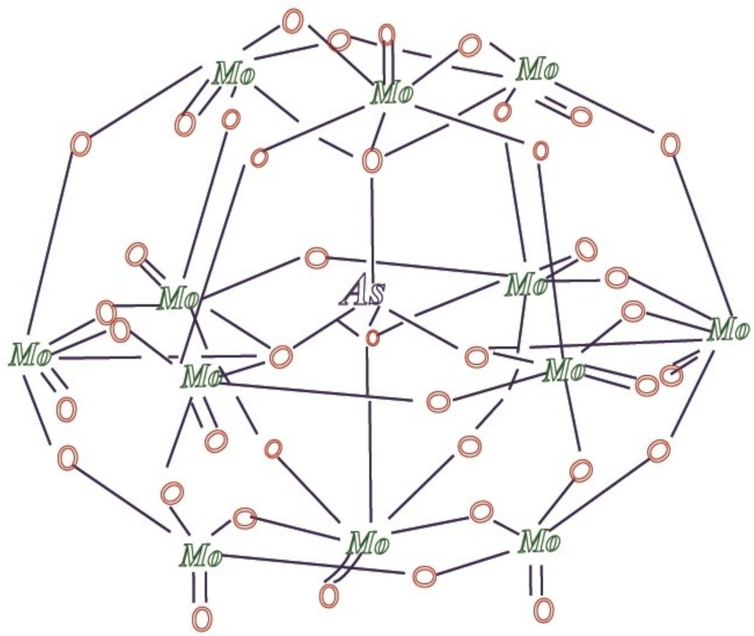

Figure S1: Structure of Arsenomolybdate blue complex [2]

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

Parameters to be optimized	Fixed Parameters					Variable Parameters	Optimum
	Temperature (°C)	Contact time (min)	pH	Adsorbent dose (mg)	Initial Arsenic concentration (mg/L)		
Solution pH	25	70	---	50	10	1.00 to 10.0	6.5 pH
Temperature °C	---	70	6.5	50	10	20 to 50 °C	35 °C
Adsorption time (min)	35	---	6.5	50	10	10 to 80.0 min	70 min
Initial Arsenic concentration (mg/L)	35	70	6.5 pH	50	10	1-20 mg/L	10 mg/L
Adsorption doze (mg)	35	70	6.5	---	10	10-70 mg/L	50 mg

Section 3

λ-max Determination of Arsenomolybdate Blue complex: First, a UV spectrophotometer was turned on, and after five minutes, a 400 nm wavelength was chosen as the initial wavelength. Then, the instrument was calibrated using distilled water for the purpose of reference solution. The sample solution was placed then in UV-spectrophotometer, and the initial absorbance at a wavelength of 400 nm was measured. After regular intervals, the absorbance was measured by keeping the difference of 10 nm. It was observed that the absorbance started to increase with time until a certain limit and after that the absorbance started to decrease .All of the absorbance measurements up to this point had been taken at regular intervals, and a graph between time and absorbance was plotted to give lambda max values of 10 ppm complex. Each sample which was comprising the untreated complex was subjected to the process and the value of absorbance constantly varied due to different concentration of As^{+5} in the solution. The maximum absorbance was recorded at 850 nm and its value is 0.825 was shown in Figure S2 [3].

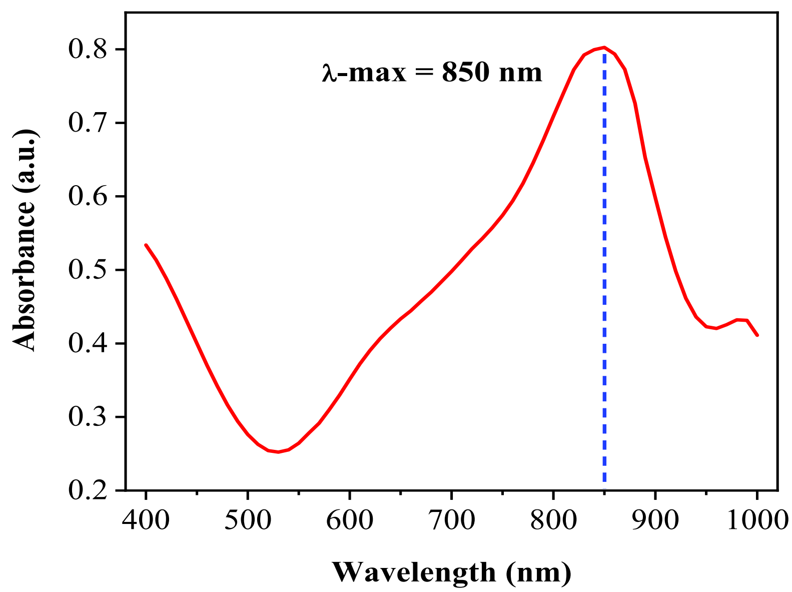

Figure S2: Lambda max of AMC.

Table S2: EDX Analysis Weight and Atomic percentage of elements in as-synthesized $CuFe_2S_xO_{4-x}$.

Elements	Wt %	At %
C	0.60	1.68
O	25.89	54.6
S	2.51	2.63
Fe	46.8	28.26
Cu	24.2	12.83
Totals	100	100

Table S3: The Comparison for adsorption capacities of $CuFe_2O_4$ and $CuFe_2S_xO_{4-x}$.

Adsorbent	**pH**	**Adsorption capacity of As (III) (mg/g)**	**Adsorption capacity of As (V) (mg/g)**	**Time**	**Reference**
$MnFe_2O_4$ NCs	-	22.27	-	-	[4]
Fe_3O_4 Particles	-	6.77	7.23	2 h	[5]
Fe_2O_3/MnO_2	6.2	2.89	3.84	12 h	[6]
$CuFe_2O_4$ (powder)	7.3	41.2	-	3 h	[7]
Fe-Cu binary oxide	7.9	122.3	82.7	24 h	[8]
$Mg_{0.27}Fe_{2.50}O_4$	5.2	127.4	83.2	12 h	[9]
$MnFe_2O_4$ (powder)	7.5	94	90	24 h	[10]
$CoFe_2O_4$ (powder)	7.0	100	74	-	[10]
Sawdust/$MnFe_2O_4$ composite	7.0	87.57	88.99	8-20 h	[11]
Fe-Ni binary oxide	-	168.6	90.1	-	[12]
Fe_2O_3	-	20	4.9	1 h	[13]
$CuFe_2O_4$ foam	6.5	44.0	85.4	3 h	[14]
$CuFe_2S_xO_{4-x}$	6.5	As^{3+} to As^{5+} (188.8 mg/g)	AMC adsorption (188.8 mg/g)	70 min	This Work
$CuFe_2O_4$	6.5	140.21 mg/g	140.21 mg/g	70 min	This Work

Table S4: Kinetic parameters: the 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 Model	Parameters		
Pseudo-first order	$K_1 = 1.854 \times 10^{-3}$	q_e (mg/g) = 449.03	$R^2 = 0.95458$
Pseudo-second order	K_2 (g/mg) = 2.029×10^{-5}	q_e (mg/g) = 476.19	$R^2 = 0.89688$
Liquid-film diffusion	$K_F = 1.0223$	--	$R^2 = 0.71585$
Intra-particle diffusion	K_d (mg/g $h^{-0.5}$) = 94.206	--	$R^2 = 0.93945$
Langmuir	K_L(L/mg) = 0.972	q_{max} (mg/g) = 188.41	$R^2 = 0.99981$
Freundlich	K_F (mg/g) = 154.84	1/n = 0.11109	$R^2 = 0.67479$
Temkin	K_T (L/mg) = 40525.55	--	$R^2 = 0.66186$

Table S5: Comparison of Langmuir, Freundlich and Temkin models parameters with reported adsorbents.

Sr.no	Adsorbent	K_F	K_L	K_T	Reference
1	Manganese ferrite nanoparticles	19.97 (L/g)	2327.91 (L/g)	-	[15]
2	Graphene oxide/$CuFe_2O_4$ foam	16.49 (mg/g)	0.046 (L/mg)	-	[16]
3	Porous copper ferrite foam	29.28 (mg/g)	0.32 (L/mg)	-	[14]
4	Novel fabricated copper ferrite	39.85	0.00025	-	[8]
5	Aluminum doped manganese copper ferrite polymer	0.853(ụg g^{-1})	-	-	[17]
6	Cobalt ferrite nanoparticles	175.56 (ụg/g)(L/ụg)$^{1/n}$	-	-	[18]
7	$CuFe_2S_xO_{4-x}$	154.84 (mg/g)	0.972 (L/mg)	40525.55 (L/mg)	This work

Section 4

Sampling from Field Station: The 25 water samples of different areas of Bahawalnagar district were collected to estimate and remove the total arsenic. The survey shows that the water taken by the hand pumps has a somewhat higher concentration of arsenic than that taken by other sources such as tube-well, motors, etc, Average 135 ppb arsenic was found in Bahawalnagar district ground drinking water which is too high then WHO limits. The results also show that in those areas where the arsenic level in drinking water is high, there are some symptoms of arsenic diseases. These were carefully examined by our team members (Ujala Quyyum, Muhammad Zeeshan Abid, and Farooq Ahmad). Arsenic contaminated water was treated with 1 g of as-synthesized $CuFe_2S_xO_{4-x}$ adsorbent to remove arsenic at optimised conditions. The adsorption capacity of as-synthesized adsorbent is 188 mg/g, and 1 g of adsorbent can make up to 365 gallons of arsenic-free water in Bahawalnagar district, where average arsenic in water is 135 ppb. The table 1 represents the estimation of arsenic in ground drinking water and treated water samples of different areas.

Section 5

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) adsorption:

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

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

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

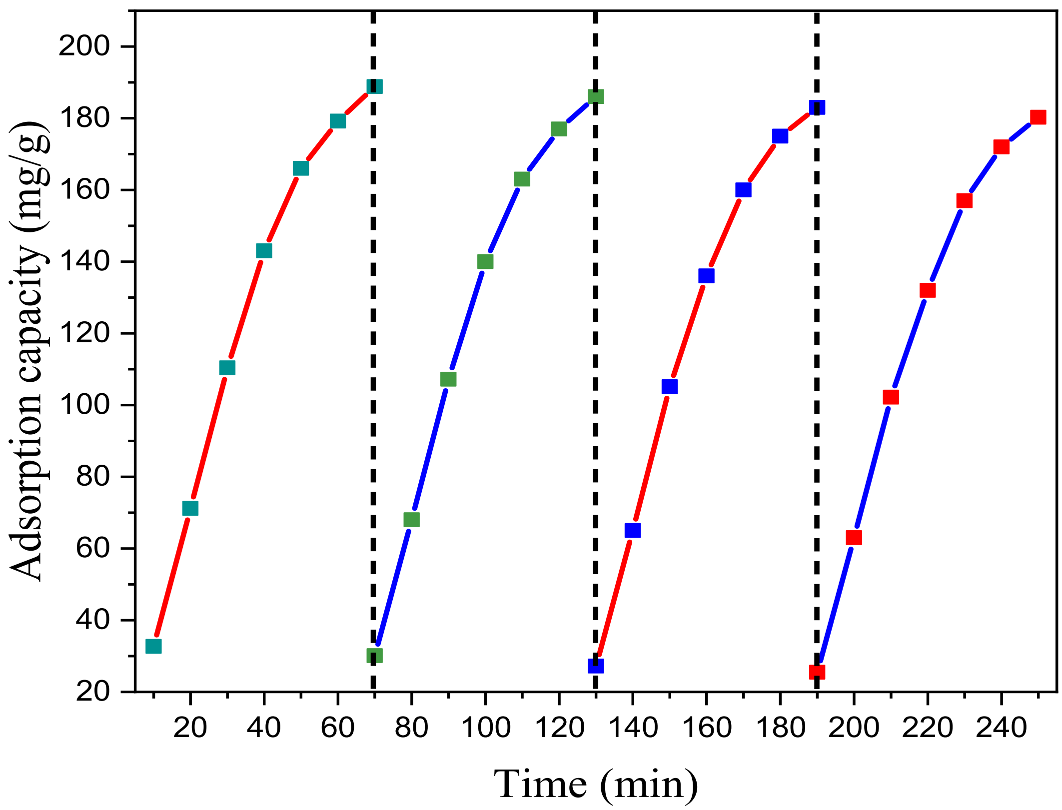

Figure S3: Reusability of $CuFe_2S_xO_{4-x}$.

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