Supporting Materials

Simple and Efficient Synthesis of Iron Oxide-Coated Silica Gel Adsorbents for Arsenic Removal: Adsorption Isotherms and Kinetic Study

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Nomenclature.

C_o ; initial arsenic concentration before adsorption process ($mg \cdot L^{-1}$)
C_e ; equilibrium arsenic concentration after adsorption process ($mg \cdot L^{-1}$)
q_e ; equilibrium adsorption capacity ($mg \cdot g^{-1}$)
q_t ; equilibrium adsorption capacity at a given time ($mg \cdot g^{-1}$)
t ; time (min)
ε ; Polanyi potential
R ; molar gas constant ($kJ \cdot mol^{-1} \cdot K^{-1}$)
T ; absolute temperature (K)
$K_{1\text{-}ads}$; pseudo-first-order rate constant (min^{-1})
$K_{2\text{-}ads}$; pseudo-second-order rate constant ($g \cdot mg^{-1} \cdot min^{-1}$).
b ; Langmuir constant related to adsorption intensity ($L \cdot mg^{-1}$)
Q_o ; Langmuir constant reflecting the theoretical maximum adsorption capacity ($mg \cdot g^{-1}$).
Q_s ; Saturated Sips model adsorption capacity ($mg \cdot g^{-1}$)
a_s ; Sips isotherm constant (dimensionless)
n_s ; Sips isotherm exponent (dimensionless)
K_F ; Freundlich constant related to adsorption capacity [$(mg \cdot g^{-1})$ $(L \cdot mg^{-1})^{1/n}$]
n ; Freundlich constant related to adsorption intensity (dimensionless)
Q_d ; Saturated Dubinin-Radushkevich model adsorption capacity ($mol \cdot kg^{-1}$),
$K_{D\text{-}R}$; Dubinin-Radushkevich constant ($mol^2 \cdot kJ^{-2}$)
$E_{D\text{-}R}$; Dubinin-Radushkevich model mean free energy of sorption ($kJ \cdot mol^{-1}$)

Iron Quantification on Iron Oxide-coated Silica Gel

A certain amount of SiO_2-Fh, SiO_2-Hm and SiO_2-Mt was dissolved in a mixture of concentrated HCl and some drops of concentrated HF with sonication for 1 h; HF and HCl were used to completely dissolve the silica supporter and iron oxide, respectively. Small volume of this mixture was then taken out and diluted 20 times with deionized (DI) water for iron content determination by ICP-AES.

Iron Oxide Phase Characterization

Pure iron oxide phases in powder form were prepared using the same method previously described in experimental section in the absence of the silica gel. Iron oxide phase was determined to be ferrihydrite, hematite and magnetite based on XRD analysis

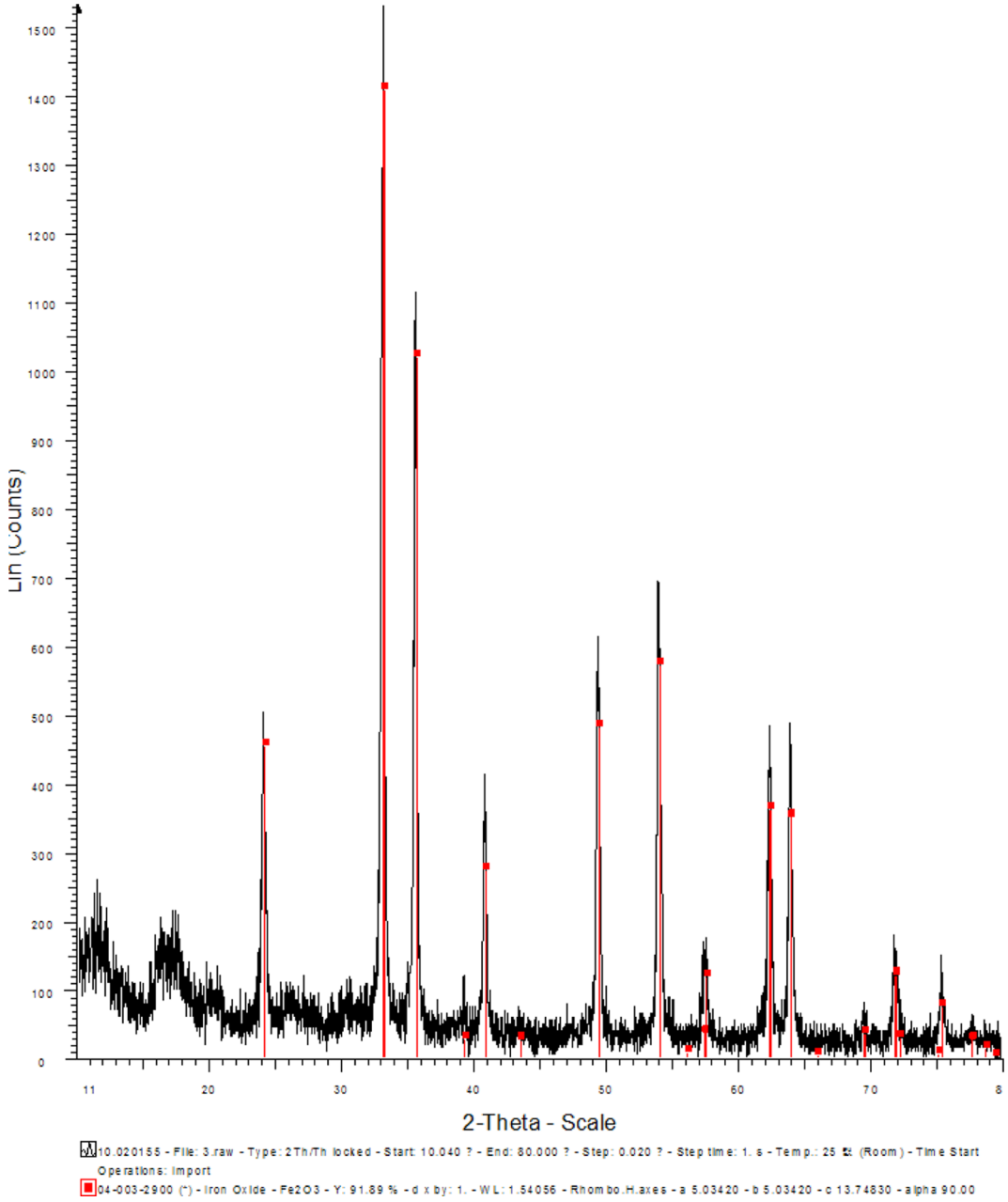

Figure S1. Powder XRD spectra of hematite sample (black) and hematite reference from JCPDS card # 04-003-2900 (red)

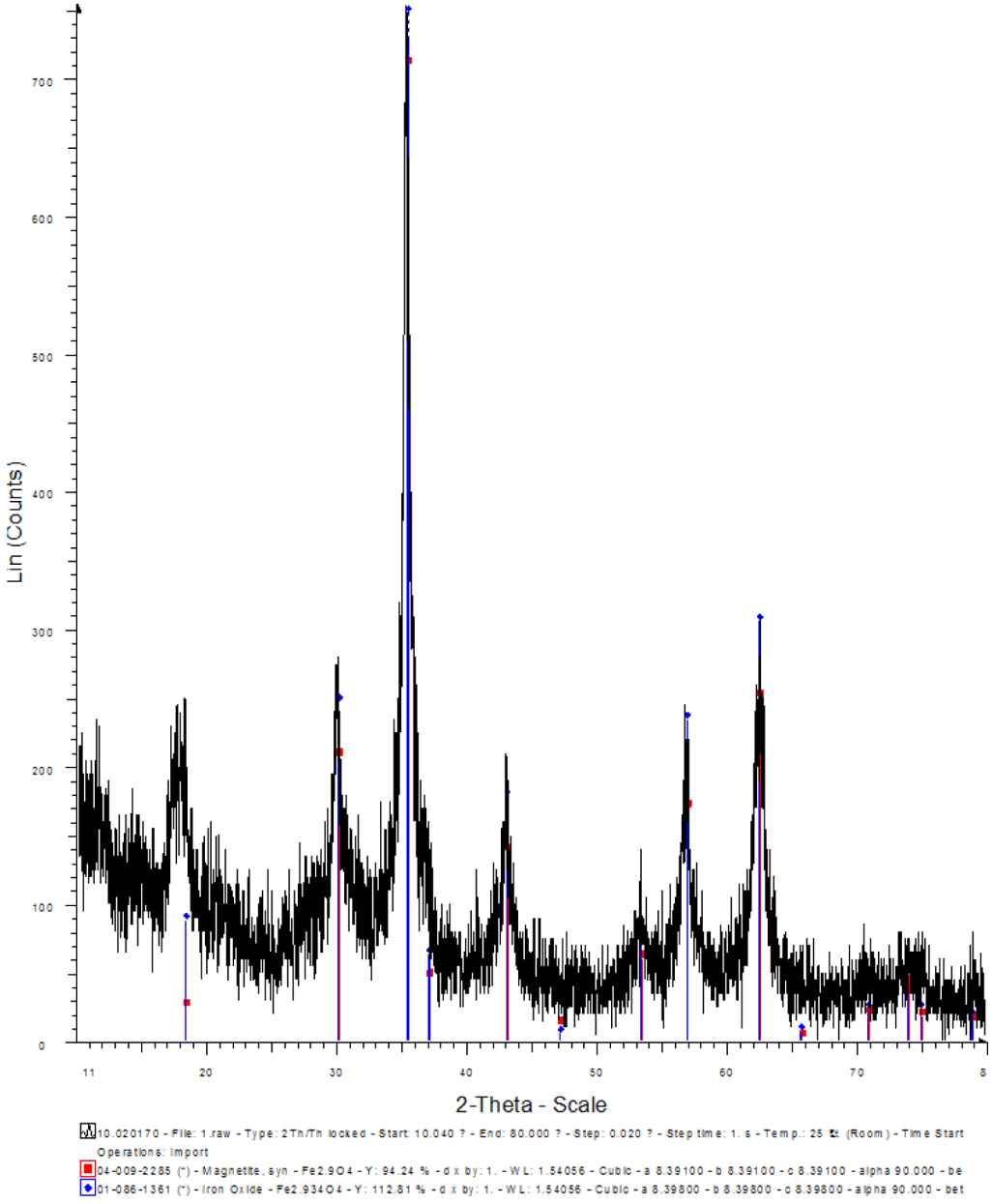

Figure S2. Powder XRD spectra of magnetite sample (black) and magnetite reference from JCPDS card # 01-076-0957 (blue) and # 01.086.1347 (red)

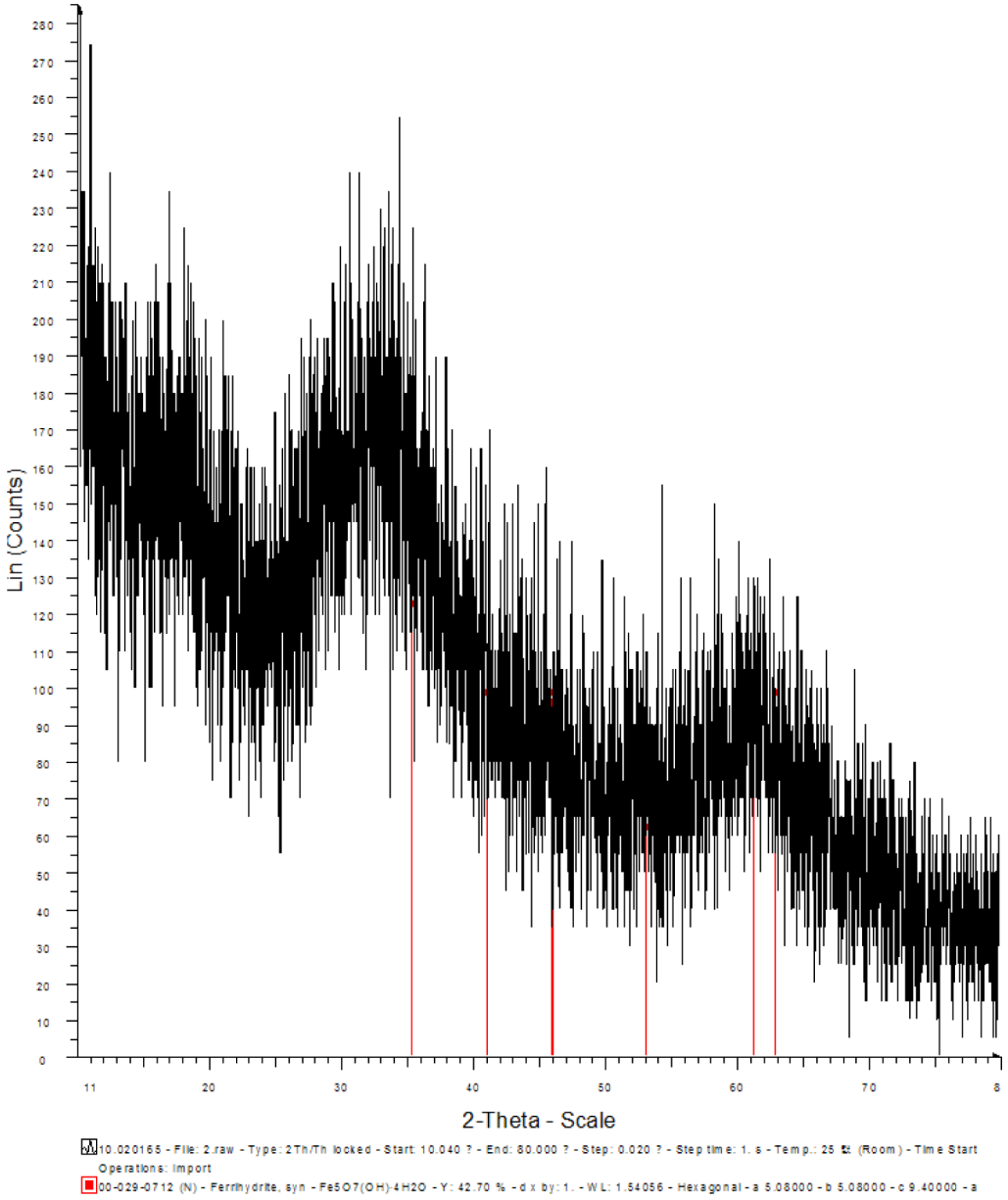

Figure S3. Powder XRD spectra of ferrihydrite sample (black) and ferrihydrite reference from JCPDS card # 00.029.0712 (red)

Arsenic Removal by Bare Silica Gel

The role of silica as supporter for iron oxide adsorbent was tested against arsenic contaminated water sample. The result showed that uncoated silica gel was not able to remove both arsenite and arsenate confirming its role as supporter in iron oxide-coated silica gel system.

Table S1. Arsenic removal by bare silica gel

	C_o (mg·L^{-1})	C_e (mg·L^{-1})	Removal (%)
Arsenite	1.130	1.127	0.26
Arsenate	1.060	1.050	0.94

BET Analysis for Determination of Surface Area and Pore Size of Bare Silica Gel

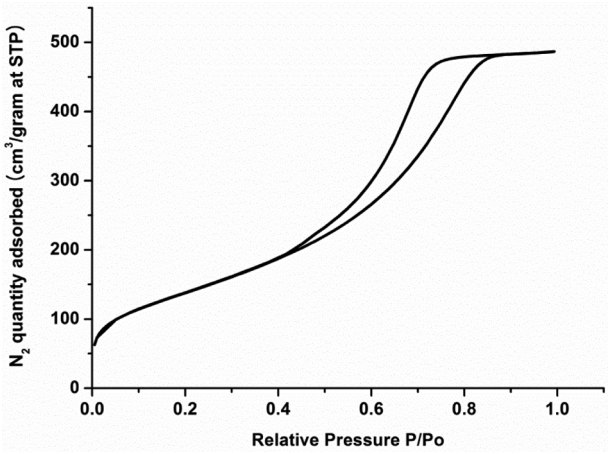

Figure S4. BET surface area measurement of uncoated silica gel.

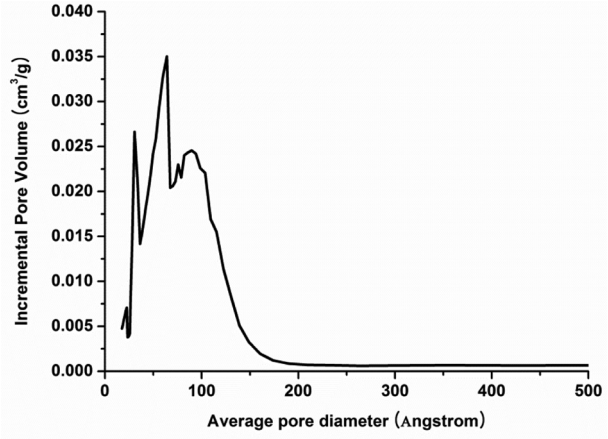

Figure S5. BET pore size measurement of uncoated silica gel.

BET Surface Area: 504.3349 m^2/g
Total pore volume: 0.753110 cm^3/g
Adsorption average pore width/size): 59.7309 Å

Determination of Rate-limiting Step During Arsenic Adsorption Onto Hematite-coated Silica Gel

The kinetic data was tested against intraparticle diffusion and liquid film diffusion model to determine the rate-determining step of arsenic adsorption onto hematite coated silica gel[1] Retention of arsenic on the active sites followed by surface complexation reaction is assumed to be very rapid and can be considered negligible. The intraparticle diffusion model assumes that solute uptake varies almost proportionally with square root of time rather than contact time (t) while neglecting the effect of pore size or radius on adsorption process. This model was widely found in many adsorption cases and is given by simple equation:

$$q_t = K_i \cdot t^{0.5} \quad (1)$$

The liquid film diffusion model states that the flow of adsorbate through the liquid film surrounding the adsorbent particle is the slowest stage in the adsorption process which determines the kinetics of the whole process and can be written as:

$$-\ln(1-F) = -\ln\left(1-\frac{q_t}{q_e}\right) = K_{lf} \cdot t \quad (2)$$

Lines from both models in Fig. S6 did not pass through the origin which implies that the rate-limiting step of arsenic adsorption process on the hematite coated silica gel might be governed by both liquid film diffusion and intraparticle diffusion simultaneously. The larger values of correlation coefficient from liquid film diffusion model suggested that arsenic adsorption onto hematite coated silica gel was mainly governed by liquid film diffusion process(more contribution toward rate-determining step) with additional contribution from intraparticle diffusion process.

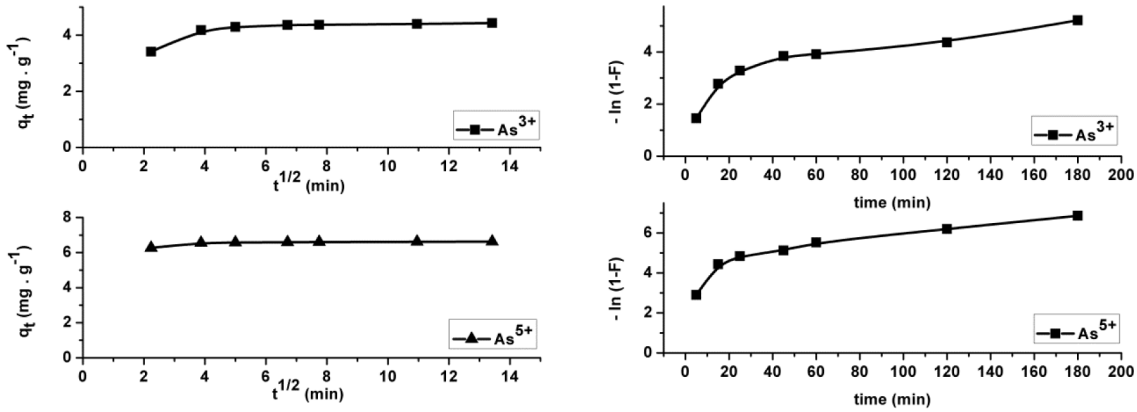

Figure S6. Intraparticle diffusion (left) and liquid film diffusion (right) model for adsorption kinetics of arsenic onto hematite-coated silica gel.

Table S2. Estimated value of intraparticle diffusion and liquid film diffusion model parameters for arsenic adsorption on hematite-coated silica gel

Kinetic model	Parameters	Arsenic species	
		As^{3+}	As^{5+}
Intraparticle diffusion	K_i ($mg \cdot g \cdot min^{0.5}$)	0.064	0.022
	R^2	0.392	0.365
Liquid film diffusion	K_{lf} (min^{-1})	0.017	0.018
	R^2	0.72	0.752

K_i intraparticle diffusion constant ($mg \cdot g \cdot min^{0.5}$)
K_{lf} liquid film diffusion constant (min^{-1})
F ratio between q_t and q_e (dimensionless)
q_t equilibrium adsorption capacity at a given time ($mg \cdot g^{-1}$)
t time (min)

Affinity of Arsenic Towards Hematite-coated Silica Gel

The affinity between adsorbent material and the adsorbate could be estimated from value of dimensionless separation factor $(R_L)^2$ which would determine the efficiency of the overall adsorption process. Separation factor is simply a ratio of unused adsorption capacity to the maximum adsorption capacity. The separation factor is related to Langmuir model adsorption intensity (b) by a simple equation:

$$R_L = \frac{1}{1 + bC_o} \quad (3)$$

The value of R_L determines whether the adsorption process is favorable or unfavorable. According to the value of R_L, the adsorption process is considered to be favorable if $0 < R_L < 1$, unfavorable if $R_L > 1$, linear if $R_L = 1$ and irreversible if $R_L = 0$. All values of separation factor are within the range of 0 and 1 suggesting the favorable adsorption for both arsenite and arsenate within the studied initial arsenic concentration. The favorability of adsorption process could also be tested from the adsorption intensity (1/n) value from Freundlich isotherm model. The 1/n value was less than unity implying favorable adsorption of both arsenite (1/n = 0.492) and arsenate (1/n = 0.253) onto the hematite-coated silica gel.[3,4]

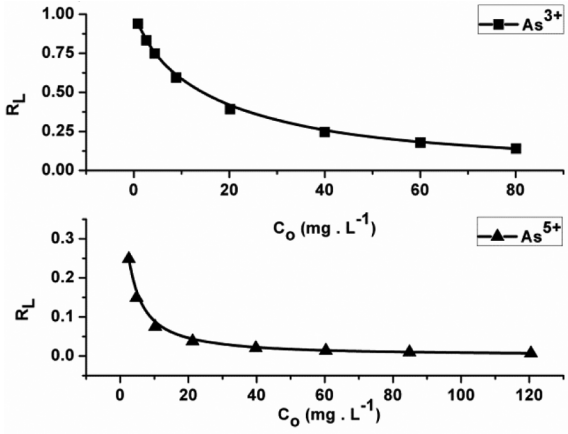

Figure S7. Affinity of arsenic toward hematite-coated silica gel was expressed in value of separation factor.

References

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4. Salim, M.; Munekage, Y. Removal of arsenic from aqueous solution using silica ceramic: adsorption kinetics and equilibrium study; *Int. J. Environ. Res.* **2009**, *3*, 13.