S1. Methodology and Design of Experimental

S1.1. Statically Optimization

In present study, RSM based Central Composite Design (CCD) used to find out the cumulative expression of four autonomous parameters: contact time (A), pH (B), 6h aged mHAP NPs dose (C) and As(III) concentration (D). CCD requires minimum number of test as the standard 2k factorial with its origin at the center, 2k points fixed axially at a distance and replicate tests at the center. The number of experiments (N) have need of CCD were calculated from equation 1.

\[ N = 2^k + 2k + kc = 2^4 + (2 \times 4) + 6 = 30 \]  

(1)

The desired range of the parameters are defined in coded form that are lie in between ±1 for the factorial points and 0 for central point.

The analysis of variance (ANOVA) was used to identify significant parameters and their individual as well as interactive effect on the As(III) removal process. Significance of process variables was checked by p-value and F-value. The correlation between anticipated response and autonomous parameters can be written in the form of equation 2.

\[ Y = f(X_1, X_2, X_3, X_4, \ldots \ldots X_k) + \epsilon \]  

(2)

where Y is the response of the system and X is the variable of action called factor, k is the number of factors being studied and \( \epsilon \) is the experimental error. Basically, CCD works between actual factor and coded factors which can be written as equation 3.

\[ \text{Coded value (} x_i) = \frac{X_i - X_{avg}}{\Delta X} \]  

(3)

where \( X_i \) is actual value of the \( i^{th} \) factor in the form actual units, \( X_{avg} \) is the average of the low and high values for the \( i^{th} \) factor and \( \Delta X \) represent the step variation. In order to find exact functional relationship between autonomous parameters and the response, a second order
polynomial equation 4 was used to describe the effect of process parameters in terms of linear, quadratic and cross product terms.

\[ Y = b_0 + \sum_{i=1}^{k} b_iX_i + \sum_{i=1}^{k} b_{ii}X_i^2 + \sum_{i<j}^{k} \sum_{j}^{k} b_{ij}X_iX_j + \epsilon \]  

(4)

where i and j are linear, quadratic coefficients; \( b_0 \) is constant coefficient and \( b_{ij} \) is quadratic coefficient. Each parameter is investigated for distinct and interactive effect on removal process of As (III). For four autonomous parameters with \( Y \) as ultimate response in their coded form, equation 4 can be decoded in equation 5.

\[ Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{14}X_1X_4 + b_{23}X_2X_3 + b_{24}X_2X_4 + b_{34}X_3X_4 + \epsilon \]  

(5)

It is required to find a suitable approximation for the true functional relationship between autonomous parameters and the response surface to optimize the response variable (\( Y \)).

**S1.2. Adsorption Isotherm**

Isotherms also defined the relationship between the amount adsorbed by a unit weight of adsorbent and the amount of adsorbate remaining in a medium at equilibrium at constant temperature. The batch experiments data were employed according to Langmuir\(^1\), Freundlich\(^2\) and Temkin\(^3\) isotherms to establish adsorption hypothesis.

Langmuir isotherm speculated homogeneous adsorption of adsorbate at specific sites of adsorbent as epitaxial deposition. Thereby, the isotherm presumed invariable energies of adsorption on to surface and resistance labiality of adsorbate in the plane of the surface. The linearity for Langmuir isotherm is expressed as equation 6,
\[
\frac{1}{q_e} = \frac{1}{q_m K_{ads}} \left( \frac{1}{C_e} \right) + \left( \frac{1}{q_m} \right)
\]  

(6)

where, \( q_e \) is the amount of adsorbed As(III) (mg/g) at equilibrium, \( q_m \) is the maximum capacity of mHAP NPs for As (III) (mg/g), \( C_e \) is the equilibrium concentration the As(III) in solution (mg/L) and \( K_{ads} \) is the Langmuir constant to measure of affinity of As(III) for mHAP NPs (mg/L).

Steadiness data obtained from the experiment was plotted between \( 1/q_e \) vs. \( 1/C_e \) to determine the values of intercept \( (1/q_m) \), slope \( (1/q_m K_{ads}) \) and constant \( K_{ads} \).

Freundlich isotherm hypothesized non-ideal multilayer affinity on heterogeneous surface. The logarithmic form of the Freundlich isotherm is expressed as equation 7:

\[
\log q_e = \log K_F + \left( \frac{1}{n} \right) \times \log C_e
\]  

(7)

where, \( C_e \) is the equilibrium concentration (mg/g), \( q_e \) is the adsorbed concentration at equilibrium (mg/g), \( K_F \) is the Freundlich constant related to adsorption capacity of mHAP NPs (mg/g) and \( n \) is the Freundlich constant analogous to adsorption intensity of mHAP NPs.

Temkin isotherm assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly with coverage shown in equation 8. Such adsorption is distinguished by a uniform distribution of the bonding energies.

\[
q_e = B_t \ln K_t + B_t \ln C_e
\]  

(8)

where, \( K_t \) is equilibrium constant corresponding to maximum binding energy (L/mg), and \( B_t \) is variation of adsorption energy (kJ/mol).

S1.3. Removal Kinetics

Lagergren pseudo-first order and pseudo-second order kinetics has been applied for removal of As (III) using 6h mHAP NPs. The Lagergren rate equation is indicated adsorbate uptake with respect to time from a solid liquid interface. The pseudo-first order kinetic of Lagergren may be expressed in following equation 9.
\[ \log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right) \times t \]  
\[ (9) \]

Where, \( q_e \) is the amount of As(III) adsorbed on mHAP NPs at equilibrium (mg/g), \( q_t \) is the amount of As(III) adsorbed on mHAP NPs (mg/g) at time \( t \) (min) and \( k_1 \) is the rate constant of pseudo-first order kinetic.

Further, the pseudo-second order kinetic of Lagergren may be manifested as following equation 10.

\[ \frac{t}{q_t} = \frac{1}{\left(k_2 \times q_e^2\right)} + \left(\frac{1}{q_e}\right) \times t \]
\[ (10) \]

Where, \( q_e \) is the amount of As(III) adsorbed on optimized mHAP NPs at equilibrium (mg/g), \( q_t \) is the amount of As(III) adsorbed on optimized mHAP NPs (mg/g) at time \( t \) (min) and \( k_2 \) is the rate constant of the pseudo-second order kinetic.

**Intra-Particle Diffusion Model**

The intra-particle diffusion (IPD) model proposed by Weber and Morris (1962) has been applied for adsorption kinetics.\(^4\) The As metal ions are transported from the bulk of the solution into the solid phase through an intra-particle diffusion process.\(^5\) The mathematical expression is given in equation 11.

\[ q_t = k_{ip} \times t^{1/2} + C_i \]
\[ (11) \]

Where, \( q_t \) is the fraction of As (III) removed (mg/g), \( k_{ip} \) is the intra-particle diffusion rate constant (mg/g min\(^{1/2}\)), \( t \) is the time (min) and \( C_i \) is the intercept.

**S1.4. Thermodynamic of As (III) Adsorption**

The evaluation of thermodynamics parameters, namely, enthalpy (\( \Delta H^\circ \)), Gibbs free (\( \Delta G^\circ \)) and entropy (\( \Delta S^\circ \)) are used to predict practical feasibility and nature of adsorption process, which are determined by following equations 12, 13 and 14.\(^6\)

\[ K_c = \frac{C_0}{C_e} \]
\[ (12) \]
\[ \ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \]  

(13)

\[ \Delta G^\circ = -RT\ln K_c \]  

(14)

Where \( K_c \) is the distribution coefficient, \( C_0 \) and \( C_e \) are the initial and equilibrium concentrations of As (III) in solution (mg/L) respectively, \( \Delta S^0 \) is the change in entropy (J/mol/K), \( \Delta H^\circ \) is the change in enthalpy (KJ/mol), \( \Delta G^\circ \) is the change in Gibbs free energy (J/mol) and \( T \) is the temperature (K), \( R \) is the gas constant (8.314 J/mol/K).

S2. Results and Discussion

S2.1. Statistical Optimization by RSM

In batch experiment, the effects of variable parameter; contact time between adsorbents and As(III) concentration with variable pH, NPs dose and As(III) concentration on percentage removal of As(III) was evaluated using CCD. Total 30 runs were required in triplicate for the CCD and the observed percentage removal of As(III) varied between 38% and 98%. Thus final equation 5 in terms of coded factors,

\[
\% \text{ Removal} = 97.17 + (6.37 \times A) - (1.71 \times B) + (9.46 \times C) - (5.96 \times D) - (0.44 \times A \times B) + (0.81 \times A \times C) - (1.06 \times A \times D) + (1.44 \times B \times C) - (0.94 \times B \times D) + (4.31 \times C \times D) - (7.93 \times A^2) - (3.43 \times B^2) - (7.68 \times C^2) - (6.68 \times D^2) 
\]

(15)

And in actual factor terms the equation 15 can be rewritten in equation 16

\[
\% \text{ Removal} = -10.04174 + (0.49917 \times \text{Contact time}) + (9.56510 \times \text{pH}) + (122.21065 \times 6h \text{ aged mHAP dose}) + (25.69010 \times \text{As(III) conc}) - (2.43056E-003 \times \text{Contact time} \times \text{pH}) + (0.060185 \times \text{Contact time} \times 6h \text{ aged mHAP dose}) - (0.029514 \times \text{Contact time} \times \text{As(III) conc.}) + (4.79167 \times \text{pH} \times 6h \text{ aged mHAP NPs Dose}) - (1.17187 \times \text{pH} \times \text{As(III) conc.}) + \]


(71.87500 \times 6h \text{ aged mHAP NPs} \times \text{Dose} \times \text{As(III) conc.}) - (9.78652 \times 10^{-04} \times \text{Contact time}^2) - \\
(0.85677 \times \text{pH}^2) - (341.20370 \times \text{Dose}^2) - (41.73177 \times \text{As(III) conc.}) \\
(16)

References