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.

$$N = 2^k + 2k + kc = 2^4 + (2 \times 4) + 6 = 30 \quad (1)$$

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.

$$Y = f(X_1, X_2, X_3, X_4, \ldots\ldots X_k) + € \quad (2)$$

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 € is the experimental error. Basically, CCD works between actual factor and coded factors which can be written as equation 3.

$$Coded\ value\ (x_i) = \frac{X_i - X_{avg}}{\Delta X} \quad (3)$$

where Xi 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 Δx 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.

$$Y = b_0 + \sum_{i=1}^{k} b_i X_i + \sum_{i=1}^{k} b_{ii} X_i^2 + \sum_{i<j}^{k} \sum_{j}^{k} b_{ij} X_i X_j + \text{€} \quad (4)$$

where i and j are linear, quadratic coefficients; b_o 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.

$$Y = b_0 + b_1 X_1 + b_2 X_2 + b_3 X_3 + b_4 X_4 + b_{12} X_1 X_2 + b_{13} X_1 X_3 + b_{14} X_1 X_4 + b_{23} X_2 X_4 + b_{34} X_3 X_4 ++ b_{11} X_1^2 + b_{22} X_2^2 + b_{33} X_3^2 + b_{44} X_4^2 \quad (5)$$

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,

$$\frac{1}{q_e} = \frac{1}{q_m K_{ads}}\left(\frac{1}{C_e}\right) + \left(\frac{1}{q_m}\right) \quad (6)$$

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:

$$log\ q_e = \log K_F + \left(\frac{1}{n}\right) \times \log C_e \quad (7)$$

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.

$$q_e = \mathrm{B}_t \ln K_t + \mathrm{B}_t \ln C_e \quad (8)$$

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.

$$log(q_e - q_t) = logq_e - \left(\frac{k_1}{2.303}\right) \times t \quad (9)$$

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.

$$\frac{t}{q^t} = \frac{1}{\left(k_2 * q_e^2\right)} + \left(\frac{1}{q_e}\right) \times t \quad (10)$$

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.

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

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 (ΔH°), Gibbs free (ΔG°) and entropy (ΔS°) are used to predict practical feasibility and nature of adsorption process, which are determined by following equations 12, 13 and 14.[6]

$$K_c = C_0/C_e \quad (12)$$

$$lnK_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (13)$$

$$\Delta G° = - RTlnK_c \quad (14)$$

Where Kc is the distribution coefficient, C_0 and C_e are the initial and equilibrium concentrations of As (III) in solution (mg/L) respectively, ΔS° is the change in entropy (J/mol/K), ΔH° is the change in enthalpy (KJ/mol), ΔG° 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,

% Removal = 97.17 + (6.37 × A)-(1.71 × B) + (9.46 × C) - (5.96 × D) - (0.44 × A × B) + (0.81 × A × C) - (1.06 × A × D) + (1.44 × B × C) - (0.94 × B × D) + (4.31 × C × D) - (7.93 × A^2) - (3.43 × B^2) - (7.68 × C^2) - (6.68 × D^2) (15)

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

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

(71.87500 × 6h aged mHAP NPs Dose × As(III) conc.) - (9.78652 E-004 × Contact time^2) - (0.85677 × pH^2) - (341.20370 × Dose^2) - (41.73177 × As(III) conc.) (16)

References

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