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Research Article

Keywords: Dolochar, Large-scale biosorption, Response surface methodology, Aspen Adsorption, Simulation

Posted Date: September 8th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-811892/v1>

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Version of Record: A version of this preprint was published at Environmental Science and Pollution Research on November 30th, 2021. See the published version at <https://doi.org/10.1007/s11356-021-17216-9>.

Process Optimization at an Industrial Scale in the adsorptive removal of Cd²⁺ ions using Dolochar via Response Surface Methodology

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Abstract:

Over the years, researchers have continuously searched for ways to achieve adsorption of heavy metal ions from the industrial effluents at lowest possible cost, which has resulted into the development of innumerable special type of low cost adsorbents, called biosorbents. While potential of many biosorbents have been explored in laboratory setup, very few studies have tried to scale up the biosorption process and predict the performance of these biosorbents in a large scale industrial setup. In this work, performance of laboratory synthesized dolochar has been investigated for adsorption of Cd²⁺ ions in a large scale process with the application of Aspen Adsorption. Moreover, the optimum values of the operating parameters (namely, flow rate, bed height and inlet metal ion concentration) that would result into maximum amount of cadmium ion adsorption (high exhaustion capacity) in minimum time (less exhaustion time) for a fixed mass of dolochar (1200 kg) have been calculated via the application of Response Surface Methodology. It was found out that, at optimum values of bed height (3.48 m), flow rate (76.31 m³/day) and inlet concentration (10 ppm), the optimized value of exhaustion capacity and exhaustion time for cadmium ion adsorption in dolochar packed bed is equal to 1.85 mg/g and 11.39 hours,

respectively. The validity of these simulation experiments can be proven by the fact that the obtained exhaustion capacity of dolochar packed beds always remained in close proximity of the experimentally obtained value of adsorption capacity of the dolochar in batch process mode (equal to 2.1 mg/g).

Keywords: Dolochar; Large-scale biosorption; Response surface methodology; Aspen Adsorption; Simulation

1. Introduction.

Heavy metal ions are one of the major pollutants that possess serious threat to the environment. Release of effluents contaminated with high concentrations of metal ions via the industries can have very toxic effect on the nature as these released metal ions can enter the food chain with the help of plants and fish. Metals ions dissolved in water get accumulated at the roots of plants and later get translocated to the edible parts of the plant (like fruits) and hence eventually enter the food chain(Ahmad et al. 2020). For a normal human body, increased concentrations of these metal ions can be very hazardous and can lead to very serious medical issues. For example, cadmium ions, which are frequently found in high concentrations in effluents of electroplating and smelting industries, can cause kidney damage and renal disorders if present in excess quantity inside the human body (Agarwal et al. 2020).Therefore, before discharging their waste streams, industries often apply a separation process where such toxic pollutants are removed(Siddiqui et al. 2021).

To achieve the separation of metal ions from the industrial effluents, adsorption has been the one of the most popular techniques due to its effectiveness and simplicity(Liao and Huang 2019). To achieve adsorption at lowest cost, researchers have continuously focused at preparation of very

low cost adsorbents and hence came the field of biosorbents(Wang and Chen 2014). Biosorbents are those adsorbents which are usually produced from commercially worthless products, i.e., from industrial waste (such as dolochar, slag, fly ash, etc.) or forestry/agricultural waste (such as neem bark, banana peels, coconut husk etc.)(Ogata et al. 2020). Many different types of biosorbents have shown high efficiency on the lab scale and dolochar is one of them. Dolochar is a carbonaceous material which can be obtained from the waste of sponge iron industries and has been tested multiple times for adsorption of heavy metal ions in a laboratory setup where it has yielded satisfactory results(Panda et al. 2011). One of the aims of this work is to predict the behavior of this biosorbent, if it is applied for metal removal on a large industrial scale.

While over the span of last 25-30 years, many biosorbents have been synthesized in lab and tested for metal removal in batch adsorption mode or small scale column setups, very few studies have worked towards commercialization of these biosorbents. Since ultimate goal is to use these biosorbents in an industrial setup, in this work, we design a dynamic large scale adsorption process whose parameters (namely flow rate, bed height and inlet metal ion concentration) have been optimized with the application of response surface methodology in order to get maximum value of bed exhaustion capacity in minimum time(and hence ensuring the maximum removal of metal ions in minimum time). This work can help in predicting and optimizing the expected behavior of any adsorbent, which is synthesized in lab, for a real industrial setup.

2. Materials and Methods

The system of cadmium ion contaminated stream flowing through the dolochar packed fixed bed adsorption column was simulated on the software Aspen adsorption V11.0. Physical properties that are crucial for execution of these simulation based experiments were taken from the literature. Bulk density, particle density and particle size of dolochar, as reported in literature, are equal to 1203 kg/m³, 2250 kg/m³ and 63 micron, respectively (Panda et al. 2011, 2014). For the application of Response Surface Methodology, software Design Expert V11.0 was used.

2.1. Aspen Adsorption

Under Aspen Adsorption, Liquid adsorption model was used to conduct the experiments. The general assumptions made in this model were (Zhang et al. 2019):

- The behavior of fluid across the column was assumed to be plug flow with axial dispersion. The value of axial dispersion was estimated with Slater correlation (Slater 1991) as represented in Equation 1, where E_z denotes axial dispersion coefficient, v_l denotes velocity of the liquid flowing through the bed, ε_i is the bed porosity, r_p is the radius of dolochar particles and Re is the Reynold's number. The liquid phase pressure as well as superficial velocity are assumed to have a constant value throughout the bed. These assumptions are valid since the quantity of metal being adsorbed is negligible in comparison to volume of liquid flowing through the bed and hence metal ion adsorption will have negligible effect on mass balance equation.

$$\frac{v_l r_p}{\varepsilon_i E_z} = \frac{0.2}{\varepsilon_i} + \frac{0.011}{\varepsilon_i} \left(\frac{Re}{\varepsilon_i} \right)^{0.48}$$

Eq (1)

- Molar concentrations are calculated from molar volumes. Ideal mixing is assumed to occur in the liquid phase, so molar volume is a linear function of composition.

88 • Isothermal conditions are applicable.

89 Figure 1 shows the adsorption process as designed in Aspen adsorption.

90

91 **Figure 1:** Adsorption process as designed in Aspen Adsorption.

92 The Discretization method used in all the simulations was Upwind Differencing Scheme 1 (UDS
93 1) which is based upon the first order Taylor series expansion. Equation (2) and Equation (3) show
94 the general differencing scheme made under UDS 1 method.

$$\frac{\partial \Gamma_i}{\partial z} = \frac{\Gamma_i - \Gamma_{i-1}}{\Delta z} \quad \text{Eq (2)}$$

$$\frac{\partial^2 \Gamma_i}{\partial z^2} = \frac{\Gamma_{i+1} - 2\Gamma_i + \Gamma_{i-1}}{\Delta z^2} \quad \text{Eq (3)}$$

UDS 1 was chosen in this work because of its unconditionally non-oscillatory, unconditionally stable nature, minimum simulation time and good accuracy. The accuracy can be further increased with increase in number of nodes. In this work, number of nodes was selected to be equal to 30.

2.1.1. Mass Balance.

Equation (4) presents the partial differential mass balance equation which was used to express the metal ion concentration in a small control volume inside the adsorbent bed, where ϵ_i is the bed porosity, E_z is the axial dispersion coefficient (m^2/s), z is the distance along the bed (m), q is the concentration of adsorbed cadmium ions onto dolochar (mg/g), C is the concentration of cadmium ions in the liquid phase, ρ_a is the bulk density and v_i is the interstitial velocity of the fluid through the adsorbent bed (Ahmed et al. 2020).

$$-\epsilon_i E_i \frac{\partial^2 c_i}{\partial z^2} + \frac{\partial}{\partial z} (v_i c_i) + \epsilon_i \frac{\partial c_i}{\partial t} + \rho_s \frac{\partial w_i}{\partial t} = 0 \quad \text{Eq (4)}$$

The first term of Equation 4 indicate dispersion forces whereas the second term denote the convective forces that are responsible for the biosorption process. The third term is to account for accumulation of the cadmium ions onto dolochar and finally the fourth term is the mass transfer term to account for the transfer of cadmium ions from liquid to a solid phase.

The bed porosity, in Equation 4, was calculated from the Equation (5), where ρ_b is the bulk density & ρ_p is the particle density.

$$\rho_b = \rho_p (1 - \epsilon_i) \quad \text{Eq (5)}$$

2.1.2. Kinetic Model

In this work, linear lumped resistance kinetic model was assumed. This model assumes that driving force for mass transfer of the components is a linear function of the components concentration in liquid phase or solid phase and can be mathematically represented by Equation 6 (Ahmed et al. 2020).

$$\frac{\partial w_k}{\partial t} = MTC_{sk} (w_k^* - w_k)$$

Eq (6)

where, w_k is the instantaneous equilibrium loading of adsorbate onto adsorbent (mg/g) and MTC is the overall mass transfer coefficient (m/s). MTC accounts for mass transfer resistance between the liquid and external adsorbent surface, and the mass transfer resistance due to pore structure of adsorbent surface. The value of MTC can be calculated from Katoka correlation (Equation 7) (Zulfadhly et al. 2001).

$$\left(\frac{1-\epsilon}{\epsilon} \right)^{1/3} \frac{k_L Sc^{2/3}}{u_f / \epsilon} = 1.85 Re'^{-2/3}$$

(Eq 7)

where, k_L represents MTC, Sc represents Schmidt number; Re' = Reynolds number; U = superficial velocity (m/s); ϵ = bed porosity.

Along with Linear lumped resistance model, solid film assumption was considered in this work since it expresses the mass transfer driving force in terms of the solid phase concentrations of the components (here, cadmium ions).

2.1.3 Isotherm

As reported in literature (Panda et al. 2011), the adsorption of cadmium ions onto dolomite process can be well described by Langmuir isotherm. Therefore, this work also assumes that adsorption

process is being governed by Langmuir isotherm (Equation 8) which is based upon three basic assumptions – i) adsorption on one site is independent of its other neighboring sites, ii) adsorption sites are homogenous&iii) monolayer adsorption takes place (Upadhyay et al. 2020).Based upon the convention of Aspen Adsorption, Equation (9) and Equation (10) can be used to calculate the isotherm parameters, where q_{max} is the adsorbate concentration on the adsorbent surface (mg/g) and k_L is the Langmuir constant (L/mg), and IP_1 and IP_2 are input parameters to Aspen Adsorption. In this work, values of q_{max} (2.02 mg/g) & k_L (0.33 L/mg) were taken from literature(Panda et al. 2011).

$$q_e = \frac{q_{max} \cdot k_L \cdot C}{1 + k_L \cdot C} \quad (\text{Eq 8})$$

$$IP_1 = \frac{q_{max}}{1000 M} \quad (\text{Eq 9})$$

$$IP_2 = 1000 k_L M \quad (\text{Eq 10})$$

2.2 Evaluation of Bed

One of the most widely used parameter for evaluation of an adsorbent bed is its exhaustion capacity(Kavand et al. 2018).In order to calculate exhaustion capacity, Equation (11) can be used, where, q_{tot}^e is the exhaustion capacity of the bed (mg/g), m is the total mass of adsorbent packed in the bed, C_t is the metal ion concentration in the exiting stream, C_o is the inlet metal ion concentration and Q is the flow rate of effluent through the bed.

$$q^e_{tot} = \frac{Q}{m1000} \int_0^t (C_0 - C_t) dt$$

Eq(11)

The evaluation of integral term in the Equation (11) has been done with the help of Origin Pro software in this work. The data points obtained from simulation experiments were plotted on Origin Pro followed by required area calculation in the graph using the *Integrator* gadget of the Origin Pro software.

2.3 Response Surface Methodology (RSM)

One of the aims of this work is to find the optimum set of exhaustion capacity (maximum) and exhaustion time (minimum) from a set of varying values of inlet metal ion concentration, bed height and flow rate. The working range of these parameters were taken to be between 1 m to 5 m for bed height, 10 ppm to 100 ppm for Cadmium ion inlet concentration and 50 m³/day to 100 m³/day for flow rate through the bed.

To achieve the desired task, Response Surface Methodology has been applied which is a method based on the fitting of mathematical models (linear, square polynomial functions and others) to the experimental results generated from the designed experiment and the verification of the obtained model by means of statistical techniques. The following steps were followed in order to reach at the set of optimum parameters(Witek-Krowiak et al. 2014):

1. Deciding upon the independent variables, working range of the independent variables and responses to be considered in the study.

2. Designing of experiments

3. Carrying out the experiments designed in step (2) in order to get results, i.e., getting responses.

4. Fitting a model to the obtained set of variable-response data.

5. Validation of the model with Analysis of Variance (ANOVA)

6. Determination of the optimum parameters set.

For designing of experiments, various experimental strategies are available such as factorial design(Cestari et al. 2008), central composite design(Oden and Sari-Erkan 2018), Box-Behnken approach(Jaafari and Yaghmaeian 2019), Plackett–Buman design etc. In this work, the experimental route has been mapped with help of central composite design (CCD) strategy due to its ability to analyze the complex interaction between the parameters with low number of experimental run requirements(Lingamdinne et al. 2018; Oden and Sari-Erkan 2018). Design Expert software has been used for applying RSM in this work.

3. Results and Discussion

3.1. Aspen Adsorption

All the simulations, conducted on Aspen adsorption, were conducted for a fixed mass of 1200 kg of dolochar (and hence 3.94 m^3 volume of the packed bed reactor). In one of the conducted experiments bed height, flow rate and inlet cadmium ion concentration was set to be equal to 3 m, $75 \text{ m}^3/\text{day}$ and 55 ppm, respectively. Since the mass of adsorbent is fixed to 1200 kgs and the bulk density of the adsorbent is taken to be 1203 kg/m^3 , the diameter of the bed was calculated to be 0.65m. The overall mass transfer coefficient, as calculated from Equation 7, was equal to 0.000137 for this case.

Post running the simulation for this system, it was found that the bed reached its breakthrough point ($C/C_0 = 0.05$) at 11.11 hours and eventually exhausted after 19 hours ($C/C_0 = 0.95$). The

concentration profile (C/C_0) was plotted against time and the resulting graph obtained has been shown in Figure 2. From the application of Equation (11), the exhaustion capacity of the bed was calculated to be 1.71 mg/g.

Figure 2: Concentration profile of the stream exiting from the dolochar packed bed when inlet metal ion concentration, flow rate and bed height were set equal to 75 m³/day, 55 ppm and 3 m respectively.

3.2. Response Surface Methodology (RSM)

For an industrial setup, it is preferable that maximum amount of effluent is treated (hence high exhaustion capacity is required) in minimum time (hence low exhaustion time is preferred). This ensures that the industry will have to bear the minimum cost for the metal ion separation process

since the run time of the equipment as well as adsorbent quantity requirement, both are being minimized. Therefore, RSM is being applied here to optimize the values of exhaustion capacity and exhaustion time as the independent variables flow rate, bed height and inlet metal ion concentration varies(Zinatizadeh et al. 2006).

3.2.1 Central Composite Design

The experiments were designed with the use of central composite design (CCD) strategy(Jiryaei Sharahi and Shahbazi 2017). The independent variables and their input range are presented in Table 1.

Table 1: Levels for CCD

Symbol	Factor	Low Level	Mid Level	High Level
A	Height (m)	1	3	5
B	Flow Rate (m ³ /day)	50	75	100
C	Inlet metal ion concentration (ppm)	10	55	100

CCD approach designed a total of 17 experiments out of which, at central point, 3 were replicates so as to measure the accuracy level of results(Zhang et al. 2016). Simulation experiments were conducted for all the designed 17 experiments in Aspen adsorption and the response variables, namely exhaustion time and exhaustion capacity, were obtained. Table 2 shows the Central Composite Design matrix and results obtained.

Table 2: Central Composite Design matrix and responses

Factors	Responses
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Run	A:Height meters	B:Flow Rate m3/day	C:Initial Conc PPM	Exhaustion Time Hours	Exhaustion Capacity mg/g
1	3	100	55	14.9	1.71
2	3	75	55	18.5	1.73
3	5	50	100	15.21	1.76
4	1	50	10	97.79	1.39
5	5	50	10	93.54	1.40
6	5	75	55	16.7	1.71
7	5	100	100	8.7	1.73
8	1	100	100	11.03	1.80
9	1	100	10	51.7	1.39
10	3	50	55	24.81	1.74
11	3	75	55	17.58	1.73
12	3	75	100	11.71	1.90
13	3	75	55	17.89	1.73
14	1	50	100	18.04	1.73
15	5	100	10	18.12	1.75
16	1	75	55	19.37	1.67
17	3	75	10	65.2	1.41

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225 **3.2.2. Analysis of Variance (ANOVA) and examination of the relationship between factors**
226 **and responses**

The regression analysis of experimental data obtained in Table 2 led to the conclusion that exhaustion time of the bed for this system can be expressed as a function of bed height, flow rate and inlet metal ion concentration via Equation (12). The same, for the case of exhaustion capacity of the bed, can be modeled by the Equation (13). Both the models obtained were analyzed and were found to be significant with the P-value less than 0.0001 in both cases. Moreover, for both the models, the lack of fit is not significant (relative to the pure error) which further proves the suitability of these models (P-value equal to 0.19 for exhaustion time model and equal to 0.57 for exhaustion capacity model). The predicted R^2 and the adjusted R^2 were close to each other as well as close to 1 for both the models which indicates that the suggested models can be good predictors of the experiments results (Refer Table 3 and Figure 3) (Kavitha et al. 2019).

$$\frac{1}{R_1} = 0.0534 + 0.0079 * A + 0.0165 * B + 0.0301 * C + 0.0062 * AB - 0.0002 * AC + 0.0039 * BC \quad (\text{Eq 12})$$

$$\sqrt{R_2} = 1.31 + 0.0031 * A - 0.0057 * B + 0.0955 * C + 0.0127 * AB - 0.0204 * AC - 0.0156 * BC - 0.0104A^2 - 0.0016B^2 - 0.0321C^2 - 0.022ABC + 0.025A^2B - 0.04A^2 + 0.0136AB^2 \quad (\text{Eq 13})$$

where, R_1 is exhaustion time (hours), R_2 is exhaustion capacity (mg/g), A is bed height (m), B is flow rate (m^3/day) and C is inlet concentration of cadmium ions (kmol/m^3).

Table 3: Fit Statistics for Exhaustion Time and Exhaustion Capacity suggested models

Response Variable	Adjusted R ²	Predicted R ²
Exhaustion Time	0.9714	0.8931
Exhaustion Capacity	0.990	0.9481

Figure 3 (a): Predicted vs Actual plot for Exhaustion Capacity

Figure 3 (b): Predicted vs Actual plot for Exhaustion Time

While it was observed that, for exhaustion time, all three factors, i.e, height, flow rate and inlet concentration were significant factors (with P-value equal to 0.0004, < 0.0001 and <0.0001, respectively), for exhaustion capacity, only inlet concentration (P-value<0.0001) and flow rate (P-value=0.002) were significant factors and bed height was less significant(P-value=0.1). The reason behind this less significant behavior of height factor could be the fact that the same mass of dolocharbiosorbent is being used in all experiments(1200 kgs). Therefore, with increase in bed height, diameter decreases and vice versa which leads to minimal change in exhaustion capacity

of the bed in response to the change in bed height. With respect to flow rate, it was found that increasing the flow rate results in decrease in both, exhaustion time as well as exhaustion capacity. The decrease in exhaustion capacity with the increase in flow rate is the result of decrease in residence time of the cadmium ions inside the bed which ceases the opportunity for the cadmium ions to reach the micro and meso pores of the dolochar particles(Simate and Ndlovu 2015). However, the decrease in exhaustion time is a favorable factor which results from the increase in the volume of contaminated stream being treated per unit time(Hernández-Hernández et al. 2017). With respect to inlet metal ion concentration, it was found that increasing the inlet metal ion concentration results in increase in exhaustion capacity and decrease in exhaustion time. Since the lumped linear resistance kinetic model has been assumed in this work (which assumes that rate of metal uptake is directly proportional to its concentration gradient), it was expected to observe that increase in metal ion concentration in the incoming stream would result in increase in exhaustion capacity. Therefore, decrease in mass transfer resistance and increase in concentration gradient with increase in inlet metal ion concentration can be attributed for the observed increase in exhaustion capacity(Sarin et al. 2006). Moreover, with the increase in the metal ion concentration, the exhaustion time decreases. This is the result of adsorption sites being exhausted early since more number of ions are entering into the system per unit time in addition to more number of ions being adsorbed due to lower mass transfer resistance(Popovic et al. 2020). Figure (4) visually represent the effect of varying factors onto the response variables.

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Figure(4):3-D contour plots to examine the relationship between the factors and responses.

3.2.3. Optimization of Variables

Based upon the models, the optimum values that would maximize the exhaustion capacity of bed and minimize the exhaustion time (hence achieve maximum cadmium ion adsorption in minimum time) were calculated with the help of a multiple response method called Desirability function(Zaferani et al. 2019). The optimum values of bed height, flow rate and inlet metal ion concentration were found to be equal to 3.48 m, 76.31 m³/day and 10 ppm, respectively. For these set of values, the predicted exhaustion time and exhaustion capacity from the model were equal to 11.55 hours and 1.87 mg/g, respectively and the desirability level was 0.835. When experiments were conducted with the same optimum values as input, the values of exhaustion time and exhaustion capacity were found to be equal to 11.39 hours and 1.85 mg/g, respectively, which is in very close approximation with the predicted values from the model and hence further justifies the preciseness of the models.

3.3. Validation of simulation with the experimental results

As can be inferred from the Table 2, the exhaustion capacity of the dolochar packed bed lies in the range of 1.3 mg/g to 1.9 mg/g. In this work the values of dolochar bulk density, particle density, particle size and isotherm parameters were taken from the work of (Panda et al. 2011). The same work tested the performance of dolochar for adsorption of cadmium in the laboratory setup as well and reported the maximum adsorption capacity of the dolocharbiosorbent for cadmium ions is equal to 2.1 mg/g. Therefore, the visible proximity between the values obtained from Aspen

adsorption and the lab based experiments shows the validity of the conducted simulation based experiments.

4. Conclusion:

This work was aimed at providing motivation for the industrialization of biosorbents for the application of heavy metal ions adsorption. Through the application of Aspen Adsorption, this work showed how the performance of a biosorbent in a real industrial process can be predicted. With the observed proximity between the exhaustion capacity of dolochar obtained from Aspen adsorption and the maximum adsorption capacity obtained from laboratory experiments, it was confirmed that Aspen Adsorption can be used as a good predictor of an adsorbent performance. Further, through the application of Response Surface Methodology, the effect of variation in column bed height, flow rate and inlet metal concentration onto the exhaustion time and exhaustion capacity of the dolochar packed bed was examined. Moreover, it was shown that how the optimum working parameters can be calculated for the dynamic adsorption process that would maximize the performance of the corresponding biosorbent in the industrial process being considered. Finally, it was found out that, for a fixed mass of dolochar biosorbent and at optimum values of bed height (3.48 m), flow rate (76.31 m³/day) and inlet concentration (10 ppm), the optimized value of exhaustion capacity and exhaustion time for cadmium ion adsorption in a dolochar packed bed is equal to 1.85 mg/g and 11.39 hours, respectively.

Acknowledgements: Authors would like to thank CSIR 22(0783)/19/EMR-II for funding. Authors would also like to thank BITS Pilani Hyderabad Campus and HBL Power Systems for facilitating this project.

To be presented in International Chemical Engineering Conference on “100 Glorious Years of Chemical Engineering & Technology” from September 17 to 19, 2021, organized by Department of Chemical Engineering at Dr B R Ambedkar NIT Jalandhar, Punjab, India (Organizing Chairman: Dr. Raj Kumar Arya & Organizing secretary: Dr. Anurag Kumar Tiwari).

List of Declarations

Ethical Approval: Not Applicable

Consent to Participate: Not Applicable

Consent for Publish: Not Applicable

Authors Contribution: UU: Simulation Studies and drafting

SG: Experimental validation

AA: Adsorbent synthesis

IS: Project mentoring and monitoring

KLA: Characterization of effluent

Funding: Sources of funding declared- CSIR under the scheme 22(0783)/19/EMR-II.

Recipient: I.Sreedhar

Availability of Data & Materials: Not Applicable

Declaration of Interest Statement

We, the authors hereby declare that there is no conflict of interest associated with this work and we adhered to all the guidelines of the journal.

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