

Optimization and Kinetic Study for the Removal of Chromium (VI) Ions by Acid Treated Sawdust Chitosan Composite Beads

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Authors' contributions

This work was carried out in collaboration between both authors. Author KMTMB designed the study, wrote the protocol and wrote the first draft of the manuscript. Author NMIA reviewed the experimental design and all drafts of the manuscript. Both the authors managed the analyses of the study and performed the statistical analysis. Both authors read and approved the final manuscript.

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ABSTRACT

Aims: To study the adsorption efficiency of acid-treated sawdust composite beads (SDCCB) for Cr(VI) ions and to optimize the process variables using Response Surface Methodology (RSM).

Study Design: Preparation of SDCCB, Characterization of SDCCB, Study of influence of variables on adsorption efficiency of SDCCB for Cr(VI) ions from aqueous solutions and optimization of process variables using RSM.

Place of Study: Department of Chemistry, Khadir Mohideen College, Adirampattinam, Tamilnadu, India.

Methodology and Results: The morphology and surface properties of the adsorbent have been characterized by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and BET analyzer. RSM has been used to optimize the process variables such as initial metal ion concentration, adsorbent dosage and pH of the solution on the performance of

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percentage removal of Cr(VI) ions and adsorption capacity of SDCCB. Various isotherm and kinetic models have been fitted with experimental data to describe the solute interaction and behaviour of rate controlled mechanism with the adsorbent in batch studies.

Conclusion: SDCCB is an effective, economic and eco-friendly adsorbent for the removal of nearly 95% of Cr(VI) from aqueous solutions. The mathematical model development and optimization for adsorption of Cr(VI) using statistical design of experiments appears to be a useful tool to predict and understanding the interaction effects between process variables. The isotherm models for the experimental data followed is in the order of Freundlich > Langmuir > Temkin isotherm for adsorption of Cr(VI) ions and adsorption kinetics fit suitably in a pseudo second order kinetic model. The activation parameters evaluated points out that the adsorption of Cr(VI) on SDCCB surface is an endothermic chemisorption process.

Keywords: Sawdust; chitosan; chromium(VI); RSM; adsorption; isotherms.

1. INTRODUCTION

Environmental pollution by discharge of industrial waste into water streams is a major problem because of their toxic nature. Among various industrial wastes, heavy metals are of great concern because of its bioaccumulation and non-biodegradable nature. Chromium(III) and chromium(VI) ions are generated from various industrial processes such as electroplating, leather tanning, mining, dyes and pigments, etc. [1,2]. Chromium(III) ions are non-toxic and play an essential role in the metabolism of plant and animals. Chromium(VI) ions are highly toxic. Intake of Cr(VI) ions leads to carcinogenetic and other health problems. The tolerance limit for the discharge of Cr(VI) ions into surface water is 0.1mg/l and in potable water is 0.05 mg/l [3]. Thus the removal of Cr(VI) ions becomes mandatory. A wide range of physical and chemical processes is available for the removal of Cr(VI) ions such as electrochemical, ion exchange, membrane filtration, reverse osmosis and chemical coagulation, adsorption, etc. [4].

Adsorption process is one of the efficient methods for Cr(VI) removal due to its simplicity, sludge-free operation, easiness in handling, availability of various adsorbents and more efficient in removal of heavy metals at lower concentration levels [5-10]. Several investigators have used different adsorbents for the removal of Cr(VI) ions such as activated carbon [11], chitosan [12], biosorbents [13], polymeric compounds [14], agricultural wastes [15,16] etc. Sawdust is one of the cheapest and abundantly available solid agricultural wastes in which it constitutes the cellulose, hemicellulose and lignin [17-20].

In recent years, surface modification was done to improve the adsorption capacity and metal-ion removal efficiency of adsorbents [21-25].

Chitosan, a biopolymer of glucosamine, has received considerable attention for the removal of transition metal ions and organic species due to its excellent metal chelating property and availability [26-28]. Amino group and hydroxyl group in chitosan molecules have great chelating ability of metal ions, which also improves the stability in acidic medium by formation of schiff bases [29,30].

Optimization of the process variables is needed to achieve the maximum adsorption capacity and removal efficiency. The conventional method of optimizing the process variables requires a very large number of experimental runs which is highly expensive and time consuming. This limitation can be overcome by the statistical experimental design, which reduces the number of experiments and provides appropriate model for process optimization. RSM is a useful method to optimize the responses shaped under the influence of process variables [31-36].

Hence, in the present study sawdust was chosen as the precursor and surface modification was done using sulphuric acid and chitosan and cross-linked with glutaraldehyde. The synthesized acid treated sawdust chitosan composite beads (SDCCB) were applied for the removal of hexavalent chromium. The optimization of process variables was done using three factor central composite experimental designs combined with RSM.

2. MATERIALS AND METHODS

2.1 Reagents

Sawdust was obtained from a local mill. Chitosan was purchased from Pelican Biotech industry, India (low molecular weight (>300kDa), 40-30% deacetylated in 1% acetic acid, viscosity 20-300 cpc). The chemicals used in this study such as

nitric acid, sulphuric acid, acetic acid, sodium hydroxide, acetone, ethanol, glutaraldehyde etc. were supplied by Merck, India. Potassium dichromate was used for the preparation of Cr(VI) stock solution. The AR grade of 1,5-diphenylcarbazide was used as complexing agent for analyzing chromium. Double distilled water was used to prepare all the solutions.

2.2 Preparation of Saw Dust Chitosan Composite Beads

A procedure similar to that followed for the preparation of cross-linked chitosan carbonized rice husk [35] was followed. Sawdust was sieved by sieve plate to obtain uniform particles of size 0.5 mm and was treated with concentrated sulphuric acid (50 ml per 10 g) for 2 h. Then it was washed with distilled water and dried in a hot air oven at 100°C. Chitosan gel was prepared by dissolving 3 g of chitosan in 100 ml of 2% acetic acid. 3 g of acid treated sawdust was added to the chitosan gel and kept in a rotary shaker for 12 h at 200 rpm. The acid treated sawdust chitosan solution was dropped into 500 ml of 0.5 M of NaOH solution which was kept for 12 h and the composite beads were washed with distilled water to remove excess NaOH. Cross-linking was done by immersing the beads in a 7.5% ethanolic solution of glutaraldehyde for 24 h and then the beads were washed and dried.

2.3 Characterization of SDCCB

The specific surface area of the adsorbent was measured by using GeminiV2.00 Micromeritics. The morphological structure was observed by Hitachi S3000H Scanning Electron Microscope. FTIR spectra were recorded using Perkin Elmer, spectrum RXI FTIR spectrophotometer to analyze the presence of cross-links in the adsorbent.

2.4 Adsorption Studies

Batch adsorption studies were conducted to determine the adsorption capacity and percentage removal of Cr(VI) ions using SDCCB. A desired quantity of SDCCB was added to 25 ml of known concentration of Cr(VI) ions and pH in a 100 ml volumetric flask and kept in a rotary shaker at an agitation speed of 200 rpm. The supernatant liquid samples were filtered and then analyzed by using Jasco UV spectrophotometer at 540 nm. Experiments were repeated in triplicates and the average percentage deviation was found to be 3 - 5%. The amount of adsorption of Cr(VI) ions at equilibrium

(henceforth referred to as adsorption capacity), q_e (mg/g) and percentage removal (%) were calculated using the Eqs. (1) and (2).

$$q_e = (C_0 - C_e)V / m \quad (1)$$

$$\text{Percentage removal} = [(C_0 - C) / C_0] \times 100 \quad (2)$$

where C_0 and C_e are the initial and equilibrium concentrations (mg/l), V is the volume of solution (l), q_e is the adsorbed quantity (mg/g), m is the weight of adsorbent (g) and C is the solution concentration at the end of the adsorption process (mg/l).

2.5 Response Surface Modelling

The standard RSM design called Central Composite Design (CCD) was applied in the present study to determine the optimum process variables for adsorption of Cr(VI) ions using SDCCB. The CCD was used for fitting a second order model which requires only a minimum number of experiments for modelling [33,34]. The CCD consists of a 2^n factorial runs (coded to the usual \pm notation) with $2n$ axial runs ($\pm\alpha, 0, 0 \dots, 0$), $(0, \pm\alpha, 0, 0 \dots, 0)$, ..., $(0, 0, \dots, \pm\alpha)$ and n_c center runs (six replicates, $0, 0, 0 \dots 0$). The number of factors (n) increases the number of runs for a complete replicate of the design which is given in Eq. 3 [35,36].

$$N = 2^n + 2n + n_c \quad (3)$$

An empirical model was developed to correlate the responses of the adsorption of Cr(VI) ions from aqueous solution using SDCCB based on second order as given by Eq. (4).

$$Y = b_0' + \sum_{i=1}^n b_i X_i + \sum_{i=1}^n b_{ii} X_i^2 + \sum_{i=1}^n \sum_{j>1}^n b_{ij} X_i X_j \quad (4)$$

where Y is the predicted response, b_0' is the constant coefficient, b_i is the linear coefficients, b_{ij} is the interaction coefficients, b_{ii} is the quadratic coefficients and X_i, X_j are the coded values.

3. RESULTS AND DISCUSSION

3.1 Characterization of Adsorbents

The prepared SDCCB adsorbent was characterized by BET, FTIR and SEM analysis.

3.1.1 BET and SEM analysis

The specific surface area of SDCCB was found to be $30\text{m}^2/\text{g}$. The cross sectional view of morphology of single SDCCB was investigated using SEM and the image is shown in Fig. 1 which gives the surface texture and porosity of the SDCCB particle. The image reveals that the particles have a very narrow size distribution, spherical shaped with very small cavities and rough surfaces. This may be due to the loading of biopolymer on insoluble materials (acid treated sawdust) which involves the suspension of

biopolymer in aqueous solution and subsequent cross-linking.

3.1.2 FTIR analysis

Fig. 2 shows the FTIR spectra of SDCCB adsorbent and the Table 1 lists the functional group and shift in the functional group of dominant peaks of SDCCB and Cr-loaded SDCCB, respectively. These shifts in the wave number indicate the adsorption of Cr(VI) ion on the surface of the SDCCB.

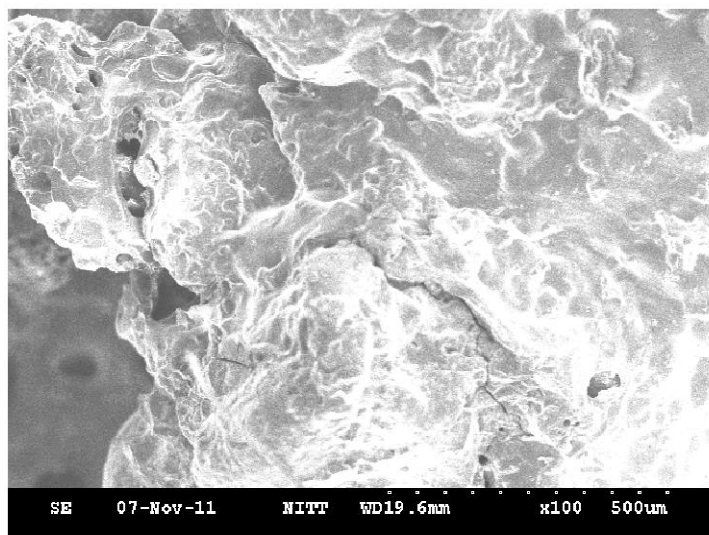


Fig. 1. SEM image of SDCCB

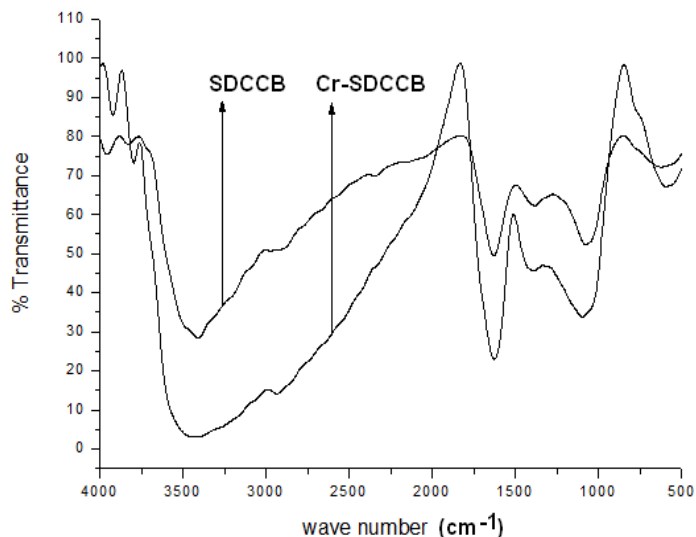


Fig. 2. FTIR spectra of SDCCB

Table 1. Functional groups present in SDCCB and Cr-loaded SDCCB

Functional groups	Functional group frequencies, cm^{-1}	
	SDCCB	Cr-loaded SDCCB
O-H (H bonded) and NH stretching	3408.4	3412.3
N-H bending vibrations	1631.1	1627.5
C-O and O-H bending	1383.6	1385.0
C-N stretching	1075.1	1097.0
NH_2 and NH wagging	622.7	594.5

3.2 Effect of Variables

Batch adsorption studies were conducted to determine the effect of pH, initial metal ion concentration, contact time and agitation speed on adsorption capacity of SDCCB for the removal of Cr(VI) ions from aqueous solution and the results are illustrated in Figs. 3 – 6.

At acidic pH, the sorption capacity is more and Cr(VI) ions exist as HCrO_4^- , CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$. The Fig. 3 shows that maximum adsorption occurs at pH 2.0 which indicates that the active form of Cr(VI) is HCrO_4^- [37,38]. In adsorption process, the initial Cr(VI) ions concentration acts as a driving force to overcome the mass transfer between the adsorbent (SDCCB) and Cr(VI) ions. In the present study, the adsorption

capacity increases from 11.9 mg/g to 101.1 mg/g and percentage removal decreases from 95% to 81% in the initial concentration ranging from 50 ppm to 500 ppm with same contact time and adsorption temperature Fig. 4. At lower concentrations of Cr(VI) there are sufficient active sites on SDCCB to occupy. However in higher concentrations of Cr(VI), they are left unadsorbed due to the saturation of binding sites for the fixed amount of SDCCB. For the optimum initial Cr(VI) concentration value of 250 ppm, (the interaction point of adsorption capacity and percentage removal, shown in Fig. 4) the percentage removal and adsorption capacity are found to be 88% and 58 mg/g respectively. It is observed from the Fig. 5 that the rate of adsorption initially increases and then gradually remains constant with increase in contact time and the equilibrium is reached nearly at 150 min for SDCCB. This may be due to the availability of a large number of vacant sites initially for adsorption, later the adsorption capacity is tailed off due to the saturation of vacant sites. Fig. 6 establishes that the rate of adsorption increases with agitation speed. The maximum 95% chromium sorption is obtained at 200 rpm beyond which the increase is not significant. This may be due to the fact that proper contact between the metal ion and active site is developed when increasing the agitation speed [39-41]. Thus increase of the agitation speed improves the diffusion of Cr ions towards the surface of the adsorbents. Hence the equilibrium agitation speed was fixed at 200 rpm.

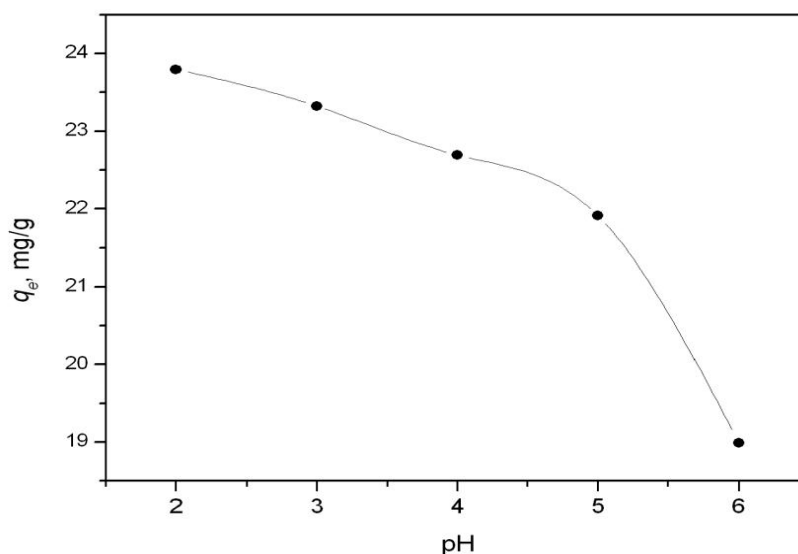


Fig. 3. Effect of pH on the Cr(VI) sorption capacity of SDCCB (Adsorbent dosage (m) = 0.1 g; Volume (V) = 25 ml; C_o = 100 ppm; Agitation speed (S) = 200 rpm)

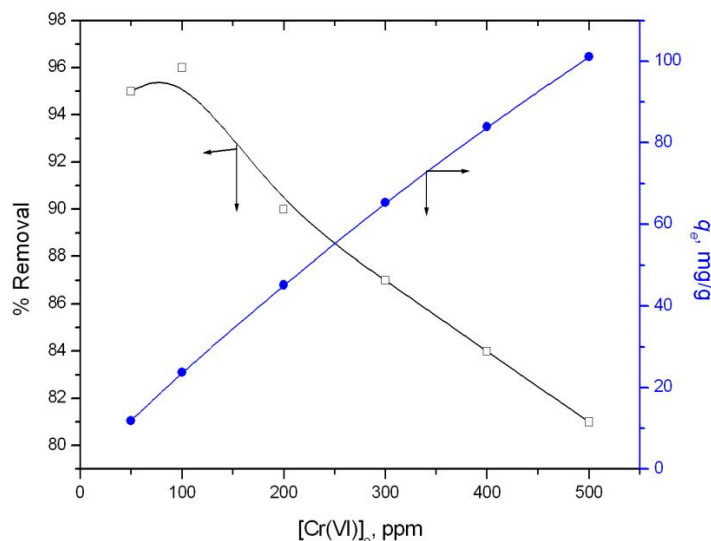


Fig. 4. Dependence of % removal and adsorption capacity on initial Cr(VI) concentration ($m = 0.1$ g; $V = 25$ ml; $S = 200$ rpm; $pH = 2.0$)

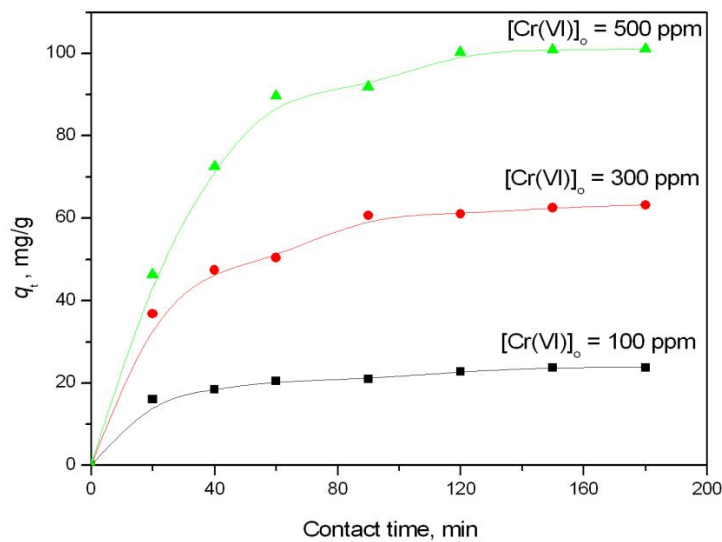


Fig. 5. Effect of contact time on the Cr(VI) adsorption capacity of SDCCB at different initial Cr(VI) concentrations ($m = 0.1$ g; $V = 25$ ml; $S = 200$ rpm; $pH = 2.0$)

The Cr(VI) adsorption capacity of SDCCB was determined at different temperatures and the results are compiled in Table 2. The results show that the uptake of Cr(VI) ions increases with increasing temperature, implying that the adsorption capacity largely depend on the chemical interaction between the functional groups on the adsorbent surface and adsorbate.

The increase in adsorption capacity may be due to the formation of some new adsorption sites on the surface of the adsorbent, the enlargement of the pores and also the increased rate of intraparticle diffusion of Cr(VI) ions into the pores of SDCCB at higher temperature, leading to the endothermic adsorption.

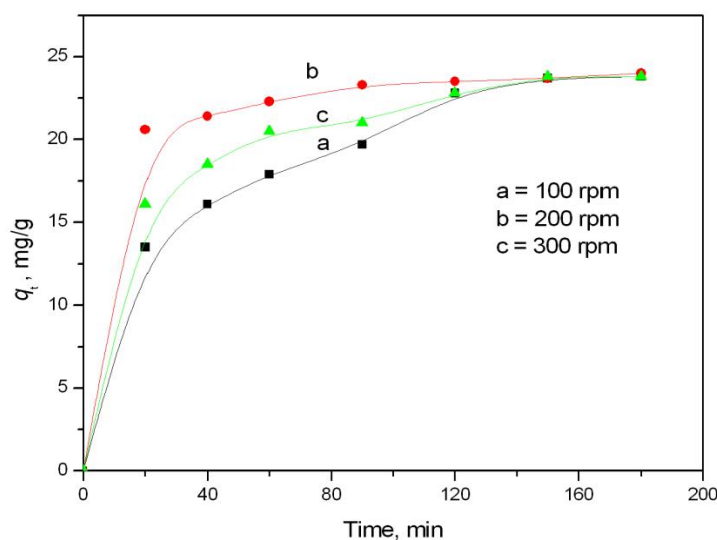


Fig. 6. Effect of agitation speed on the Cr(VI) adsorption capacity of SDCCB
($m = 0.1$ g; $V = 25$ ml; $C_o = 100$ ppm; $pH = 2.0$)

Table 2. Effect of temperature on the Cr(VI) sorption capacity of SDCCB

T, K	C_e , ppm	% removal	q_e , mg/g	$K = q_e/C_e$
303	9.6524	95.2	47.6	4.93
313	6.5071	96.7	48.4	7.43
323	3.2729	98.4	49.2	15.03
333	1.6171	99.2	49.6	30.67
343	1.2729	99.4	49.7	39.03

Conditions: $m = 0.1$ g; $V = 25$ ml; $C_o = 100$ ppm; $S = 200$ rpm; $pH = 2.0$

The ΔG° , ΔH° and ΔS° values calculated at 303 K are -4.02 kJ/mol, 48.05 kJ/mol and 171.32 J/K.mol, respectively and the energy of activation ($E_a = \Delta H^\circ + RT$) is 50.6 kJ/mol. These thermodynamic parameters can be explained on the chemical bonding nature of the adsorbent-adsorbate interaction [28,42]. The E_a value greater than $+42$ kJ/mol points out that the adsorption process here is a chemically-controlled one [43]. The negative ΔG° and positive ΔH° and ΔS° indicate that this adsorption is a feasible, spontaneous, endothermic, increased randomness and chemisorption.

3.3 Adsorption Isotherms

In the present study, various isotherm equations [40,44] like Langmuir, Freundlich and Temkin were used to describe the equilibrium characteristics of adsorption of chromium by SDCCB. Langmuir isotherm indicates surface homogeneity and monolayer adsorption. This is also analyzed by separation factor, R_L which is between 0 and 1 for favourable adsorption.

Freundlich isotherm is an indication of surface heterogeneity and multilayer sorption. Temkin model considers the effects of adsorbent-adsorbate interaction. The linearized form of these isotherms were applied to the adsorption of Cr(VI) onto SDCCB and the constants obtained from the slope and intercept of the plots have been compiled in Table 3.

Based on R^2 values, the order of isotherm for the SDCCB is: Freundlich > Langmuir > Temkin, (i.e.) multilayer lateral adsorption on heterogenic surface is possible. The maximum adsorption capacity of Cr(VI) ions is confirmed by the higher values of θ , K_L , K_F and B.

3.4 Adsorption Kinetics

The pseudo first order, pseudo second order and simple Elovich kinetic models were tested to investigate the rate of adsorption process of Cr(VI) by SDCCB. The relevant data for the analyses are shown in Table 4 and the values of constants derived from the linear plots are listed in Table 5. Based on R^2 values, the pseudo second order kinetics seems to be best suitable model for the adsorption of Cr(VI) on SDCCB. The validity of pseudo second order and Elovich models supports the fact that chemisorption is the rate limiting step in the adsorption process [28].

3.5 Adsorption Mechanism

The mechanism for the mass transfer from Cr(VI) ion to SDCCB surface follows three steps [45]:

- External mass transfer of Cr(VI) ions from the bulk fluid to the film surrounding the SDCCB adsorbent.
- From film to the adsorbent surface (i.e.) intraparticle diffusion
- From surface to the internal sites followed by binding of metal ions to the active sites (i.e.) chemisorptions.

multi-layerly adsorbed with the formation of surface ion-exchange complex between electron accepting sites of SDCCB and chromium oxy anions (electron donating nature). The ions then diffuse into the pores slowly due to chemisorptions with active sites of adsorbent. This is the rate-controlling step. This is evidenced by Elovich kinetics and activation parameters. Finally, the equilibrium is reached due to bonding with binding centres of surface functionality of the SDCCB. The adsorption mechanisms is shown in the following equations: (Ion exchange only)

Generally it is observed that the rate of adsorption process is controlled by either step (ii) or (iii). In aqueous solution at pH 2, the active forms of Cr(VI) ions are HCrO_4^- . The negatively charged active species of metal ions may be

Table 3. Summary of parameters for various isotherm models

Isotherm model	Equation	Constants for SDCCB
Langmuir isotherm	$\frac{C_e}{q_e} = \frac{1}{b\theta} + \frac{C_e}{\theta}$ $K_L = (\theta.b)$ $R_L = 1/(1 + bC_0)$	θ (mg/g) = 122.3 b (L/mg) = 0.038 K_L (L/g)= 4.69 $R_L = 0.207$ $R^2 = 0.966$
Freundlich isotherm	$\ln q_e = \ln K + \frac{1}{n} \ln C_e$	$n = 1.8$ K_F (L/g) = 8.74 $R^2 = 0.974$
Temkin isotherm	$q_t = B \ln K_T + B \ln C_e$	$B = 22.9$ K_T (L/g) = 0.58 $R^2 = 0.960$

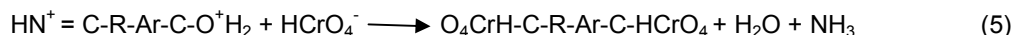
Table 4. Data for various adsorption kinetic models

Time, min	q_t , mg/g	q_e , mg/g
20	16.1	23.8
40	18.5	23.8
60	20.5	23.8
90	20.96	23.8
120	22.79	23.8
150	23.75	23.8
180	23.8	23.8

Conditions: $m = 0.1$ g; $V = 25$ ml; $S = 200$ rpm; $C_0 = 100$ ppm; $pH = 2.0$

Table 5. Summary of parameters derived for various kinetic models

Kinetic model	Equation	Constants	Value
Pseudo first order	$\ln\left(\frac{q_e}{q_e - q_t}\right) = k_1.t$	$10^2 k_1$, 1/min R^2	3.38±0.79 0.819
Pseudo second order	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	$10^3 k_2$ (g/mg/min) q_e (mg/g) R^2	2.56±0.07 25.73±0.53 0.996
Simple Elovich	$q_t = \beta \ln(\alpha\beta) + \beta \ln t$	β (g/mg) α (mg/g/min) R^2	3.62±0.20 1.19±0.13 0.984



where R and Ar is the matrix of surface-modified sawdust-chitosan composite beads containing functional groups such as imine, hydroxyl, ether of polysaccharides, phenol group of lignin and hemicelluloses. The cross-linking in chitosan reduces the number of protonated amino groups and changes the crystallinity [46,47]. So the surface acidity behaviour is responsible for such kind of adsorption [48].

3.6 Regeneration Studies

Desorption studies were also conducted to explore the feasibility of recycling the SDCCB adsorbent and recovery of the metal resources [49]. NaOH was used for the stripping section for Cr(VI) ions. Desorption experiments were conducted by mixing 0.5 g of spent adsorbent with 25 ml of 1 M NaOH. In order to determine the reusability, the adsorbent was taken out from the solution and washed with double distilled water and protonated with 0.1 M HCl. Consecutive adsorption and desorption studies were repeated several times by using the same adsorbent. The results in terms of percentage removal are shown in Table 6, which indicate the stability of the adsorbent.

Table 6. Results of regeneration studies with SDCCB for adsorbing Cr(VI) ions

Cycle no.	Cr(VI) sorption capacity of SDCCB, %
1	95.6
2	95.1
3	94.2
4	90.6
5	85.1
6	76.3

Conditions: $m = 0.5$ g; $V = 25$ ml; $C_o = 100$ ppm; $S = 200$ rpm; $pH = 2.0$

The % removal and hence the adsorption capacity decreases slightly after each cycle and even after the sixth cycle, SDCCB possesses 76.3% adsorption capacity. The recovery experiments show that metal ions are retained by the matrix in nonlabile forms and that the acid-base reactions are more effective for their displacement than complexation processes.

3.7 RSM - Development of Regression Model Analysis

In the present investigation, the CCD of three variables such as adsorbent dosage (g), pH and initial concentration (ppm), each with five levels (± 1 for the factorial points, 0 for the centre points

and $\pm\alpha$ for the axial points) were chosen as independent variables with designated coded factors as A, B and C respectively and the variables are presented in Table 7.

A total of 20 experiments were necessary to estimate the coefficients of each model using linear regression analysis. The two- dependent output responses viz. percentage removal (Y_1) and adsorption capacity (mg/g) (Y_2) were obtained from the independent input variables for CCD and are presented in Table 8.

The different polynomials suggested by the software for percentage removal (Y_1) of Cr(VI) ions and adsorption capacity (Y_2) of SDCCB are reported in Tables 9 and 10 respectively and the quadratic model is found to better represent the present results.

Table 7. Variables and levels considered for Cr(VI) adsorption using SDCCB by CCD

Factors	Code	Range and levels (coded)				
		-2	-1	0	+1	+2
Adsorbent dosage (g)	A	0.05	0.09	0.13	0.16	0.2
pH	B	2	3	4	5	6
Initial concentration (ppm)	C	100	200	300	400	500

Table 8. Experimental design matrix and responses for Cr(VI) adsorption using SDCCB

Runs	A, g	B	C, ppm	Y_1	Y_2 , mg/g
1	0.09	3	200	86.9	48.3
2	0.16	3	200	97.8	30.6
3	0.09	5	200	53.1	29.5
4	0.16	5	200	92.2	48.8
5	0.09	3	400	58.9	65.5
6	0.16	3	400	76.8	48.0
7	0.09	5	400	45.4	50.5
8	0.16	5	400	76.0	47.5
9	0.05	4	300	32.9	49.4
10	0.2	4	300	96.0	36.0
11	0.13	2	300	89.7	51.7
12	0.13	6	300	66.7	38.4
13	0.13	4	100	99.9	19.2
14	0.13	4	500	51.2	49.3
15	0.13	4	300	84.0	48.3
16	0.13	4	300	84.0	48.3
17	0.13	4	300	84.0	48.3
18	0.13	4	300	84.0	48.3
19	0.13	4	300	84.0	48.3
20	0.13	4	300	84.0	48.3

Table 9. Model summary statistics for percentage removal of Cr(VI) using SDCCB

Source	Standard deviation	R ²	Adj R ²	Predicted R ²	PRESS	Comments
Linear	8.37	0.8331	0.8018	0.7286	1821.06	
2F1	8.00	0.8760	0.8188	0.6949	2046.79	
Quadratic	3.74	0.9792	0.9605	0.8667	1115.9	Suggested
Cubic	1.84	0.9976	0.9904	0.3753	4191.4	Aliased

Table 10. Model summary statistics for adsorption capacity of SDCCB

Source	Standard deviation	R ²	Adj R ²	Predicted R ²	PRESS	Comments
Linear	5.38	0.7804	0.7392	0.6200	802.17	
2F1	5.08	0.8410	0.7676	0.6852	664.54	
Quadratic	1.80	0.9847	0.9710	0.8735	266.92	Suggested
Cubic	0.86	0.9979	0.9934	0.5722	903.02	Aliased

The quadratic model obtained for the percentage removal (Y_1) of Cr(VI) ions and adsorption capacity (Y_2) of SDCCB in terms of coded factors is reported as:

$$Y_1 = 83.61 + 14.044A - 6.23B - 10.64C + 5.11AB - 0.19AC + 3.14BC - 5.08A^2 - 1.65B^2 - 2.31C^2$$

$$Y_2 = 48.48 + 4.11A - 3.93B - 8.41C + 3.94AB - 0.26AC + 0.64BC - 1.31A^2 - 0.71B^2 - 3.42C^2$$

The analysis of variance corresponding to the two quadratic equations are reported in Tables 11 and 12 respectively.

Table 11. Analysis of variance (ANOVA) for response surface quadratic model for percentage removal of Cr(VI) using SDCCB

Source	Sum of squares	df	Mean square	F value	P value	Comments
Model	6569.92	9	729.99	52.29	<0.0001	significant
A	3155.63	1	3155.63	226.02	<0.0001	
B	621.26	1	621.26	44.5	<0.0001	
C	1812.63	1	1812.63	129.8	<0.0001	
AB	209.10	1	209.10	14.98	0.0031	
AC	0.28	1	0.28	0.020	0.8900	
BC	78.75	1	78.75	5.64	0.0389	
A ²	649.89	1	649.89	46.55	<0.0001	
B ²	68.17	1	68.17	4.88	0.0516	
C ²	134.06	1	134.06	9.6	0.0113	
Residual	139.61	10	13.96			
Lack of fit	139.61	5	27.92			
Pure error	0.000	5	0.000			
Cor.. total	6709.54	19				

In general, the ' $S_{statistics}$ ' value with low probability (P) value represents high significance of the regression model. The model F-values of 52.29 and 71.66 imply that the model is significant for percentage removal and adsorption capacity respectively. For percentage removal A, B, C,

AB, BC, A², C² are significant model terms. For adsorption capacity, A, B, C, AB, A², C² are significant model terms. Values greater than 0.1000 indicate the model terms are not significant.

Table 12. ANOVA for response surface quadratic model for adsorption capacity of SDCCB

Source	Sum of squares	df	Mean square	F value	P value	Comments
Model	2078.49	9	230.94	71.66	<0.0001	significant
A	269.78	1	269.78	83.71	<0.0001	
B	246.8	1	246.8	76.58	<0.0001	
C	1130.64	1	1130.64	350.81	<0.0001	
AB	124.03	1	124.03	38.48	0.0001	
AC	0.55	1	0.55	0.17	0.6879	
BC	3.25	1	3.25	1.01	0.3389	
A ²	43.07	1	43.07	13.36	0.0044	
B ²	12.76	1	12.76	3.96	0.0746	
C ²	294.3	1	294.3	91.31	<0.0001	
Residual	32.23	10	3.23			
Lack of fit	32.23	5	6.45	201.83	<0.0001	
Pure error	0.000	5	0.000			
Cor. total	2110.72	19				

3.8 Actual and Predicted Values

Based on quadratic equations obtained for Y_1 and Y_2 , the actual and predicted values for both the parameters were calculated and tabulated in Table 13.

The correlations between the two values for percentage removal and adsorption capacity of Cr(VI) ions using SDCCB are depicted in Fig. 7 ($R = 0.98954$; s.d. = 2.75611; $n = 20$; $P < 0.0001$) and Fig. 8 ($R = 0.9647$; s.d. = 2.59447; $n = 20$; $P < 0.0001$). The values of R^2 and R^2_{adj} were found to be 0.9792 and 0.9605 for percentage removal and 0.9306 and 0.9710 for adsorption capacity of Cr(VI) ions using SDCCB.

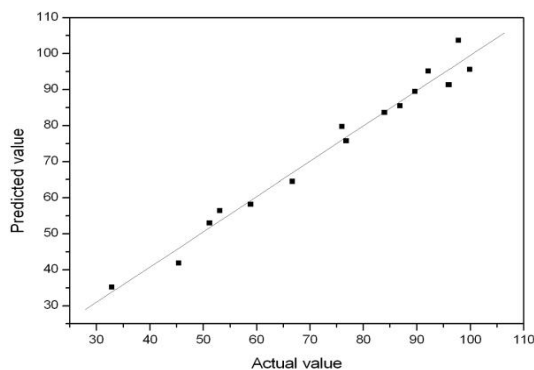


Fig. 7. Correlation between the actual and predicted values of % removal of Cr(VI) using SDCCB

3.9 Interaction Effects of Process Variables

The interaction effect of process variables for percentage removal of Cr(VI) ions and

adsorption capacity of SDCCB were visualized through three dimensional views of response surface plots and are shown in Figs. 9-11.

3.9.1 The combined effect of pH and adsorbent dosage

The combined effect of pH and adsorbent dosage on Cr(VI) percentage removal and adsorption capacity of SDCCB is shown in Figs. 9(a) and 9(b) respectively. The maximum percentage removal and adsorption capacity were obtained at pH 2. This may be due to the fact that the positive functional groups on the surface of the SDCCB adsorbent carry the oxyanions (CrO_4^{2-}) of Cr(VI) ions by electrostatic force of attraction. At higher pH, the increased negative charges on the adsorbent surface decrease the attraction of oxyanions on the adsorbent. The maximum percentage removal of 89.5% and adsorption capacity of 53.5 mg/g were observed at pH of 2, constant initial concentration of 300 ppm and adsorbent dosage of 0.13 g.

3.9.2 The combined effect of initial metal ion concentration and adsorbent dosage

Figs. 10(a) and 10(b) indicate the combined effect of initial metal ion concentration and adsorbent dosage on percentage removal and adsorption capacity of SDCCB respectively. The adsorption capacity decreases, while percentage removal of Cr(VI) ions increases, with increased adsorbent dosage. The decrease in adsorption capacity may be attributed to the shortage of metal ion concentration in the solution since the initial metal ion concentration is kept constant for all varying dosages. The increase in percentage removal may be due to the complete utilization of

Table 13. Actual and predicted values of Y_1 and Y_2

S. no.	% Removal		Adsorption capacity	
	Actual value	Predicted value	Actual value	Predicted value
1	86.9	85.46	48.3	44.35
2	97.8	103.7	30.6	31.29
3	53.1	56.5	29.5	29.87
4	92.2	95.19	48.8	42.55
5	58.9	58.27	65.5	67.92
6	76.8	75.76	48	43.8
7	45.4	41.86	50.5	45.98
8	76	79.8	47.5	47.62
9	32.9	35.18	49.4	50.33
10	96	91.36	36	38.9
11	89.7	89.48	51.7	52.3
12	66.7	64.56	38.4	41.63
13	99.9	95.66	19.2	21.85
14	51.2	53.08	49.3	50.48
15	84	83.61	48.3	48.94
16	84	83.61	48.3	48.94
17	84	83.61	48.3	48.94
18	84	83.61	48.3	48.94
19	84	83.61	48.3	48.94
20	84	83.61	48.3	48.94

Table 14. Optimized process variables value for adsorption of Cr(VI) ions by SDCCB

Adsorbent dosage (g/100ml)	Initial metal ion concentration (mg/l)	pH	% Removal		Adsorption capacity (mg/g)	
			Predicted	experimental	Predicted	experimental
0.36	200	2	95	94.6	53.4	53.0

all active sites in the adsorbent by metal ions. The maximum percentage removal of 83.6% and adsorption capacity of 48.5 mg/g were obtained at constant pH of 4, initial concentration of 300 ppm and 0.13 g of adsorbent dosage.

3.9.3 The combined effect of initial metal ion concentration and pH

Figs. 11(a) and 11(b) represent the combined effect of initial metal ion concentration and pH on percentage removal and adsorption capacity respectively. The adsorption capacity of SDCCB increases, while the percentage removal of Cr(VI) ions decreases, with increased metal ion concentrations. The increase in adsorption capacity may be due to the higher adsorption rate and utilization of all active sites available for the adsorption at higher concentration. The decrease in percentage removal may be due to the limited number of active sites as the adsorbent attained saturation above certain concentration. The maximum percentage removal of 95% and adsorption capacity of 45.2 mg/g were obtained at pH of 3, initial

concentration of 247 ppm and adsorbent dosage of 0.13 g.

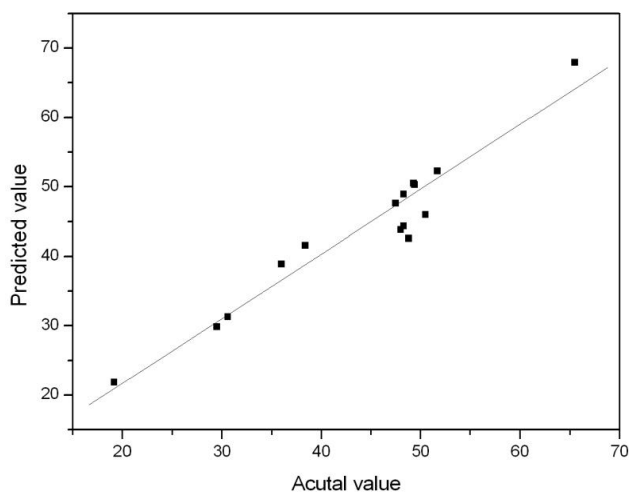
The predicted and the experimental optimum conditions of the process variables for the maximum percentage removal and adsorption capacity are shown in above Table 14.

3.10 Comparison of SDCCB with Other Adsorbents

The chemical modification in general improves the adsorption capacity of adsorbents probably due to higher number of active binding sites after modification, better ion-exchange properties and formation of new functional groups that favours metal uptake [50]. The biosorption capacity of modified composite bead of sawdust for Cr(VI) (present study) is higher than the majority of the treated or untreated sawdust Table 15. In general, the bead form significantly enhances the diffusion properties of Cr(VI) ions because of expansion of cellulosic matrix. So the composite beads exhibit a twofold or more increase in the adsorption capacity of Cr(VI) ion.

Table 15. Comparison of Cr(VI) adsorption capacity of SDCCB with other adsorbents

S. no.	Adsorbent	Retention efficiency of Cr(VI)	References
1	Chitosan flakes	22.09 mg/g	[51]
2	Fe-cross-linked chitosan complex	295 mg/g	[52]
3	Oil Palm Shell Charcoal	Acid treated : 44.68 mg/g Chitosan coated: 52.68 mg/g Acid treated-Chitosan coated: 60.25 mg/g	[41]
4	Chemically modified plant wastes	i) High affinity for heavy metal remediation ii) improved adsorption capacity than unmodified forms	[50,53]
5	Activated carbon from coir pith	quantitative removal	[54]
6	Chemically treated Helianthus annuus	53.8 mg/g	[34]
7	Sugarcane bagasse	effective removal	[2]
8	Bagasse pretreated with NaOH and acetic acid	90%	[55]
9	Neem leaf powder	62.97 mg/g	[38]
10	Treated Tamarind wood carbon	90%	[32]
11	Sawdust granular activated carbon	> 66%	[56]
12	Neem sawdust & mango sawdust	58.82 & 37.73 mg/g	[57]
13	Treated rubber wood sawdust	44.05 mg/g	[58]
14	Treated sawdust of sal tree	9.35 mg/g	[59]
15	Treated sawdust of Indian rosewood	10 mg/g	[60]
16	Modified Oak sawdust	84% at pH 3	[61]
17	Pyrolysed sawdust	removal increases with increase in temperature	[39]
18	Modified coconut husk	Acid treated: 96% at pH 5 Base treated: 40%	[62]
19	SDCCB	122.3 mg/g; 95% at pH 2.0	Present study

**Fig. 8. Correlation between the actual and predicted values of Cr(VI) adsorption capacity of SDCCB**

It can be observed that a pH of 2.0 for Cr(VI) seems to be an optimum in nearly all cases whatever be the method of activation. Further, the activated carbon produced from sawdust compares well with the activated carbons from most of the raw materials listed in the Table 15. The high adsorption capacity of few raw

materials can be attributed primarily to the initial carbon content, activation process as well as the pore development due to the basic morphology of the raw material. Thus, the comparison establishes that SDCCB can be considered to be a viable adsorbent for the removal of Cr(VI) ions from dilute solutions.

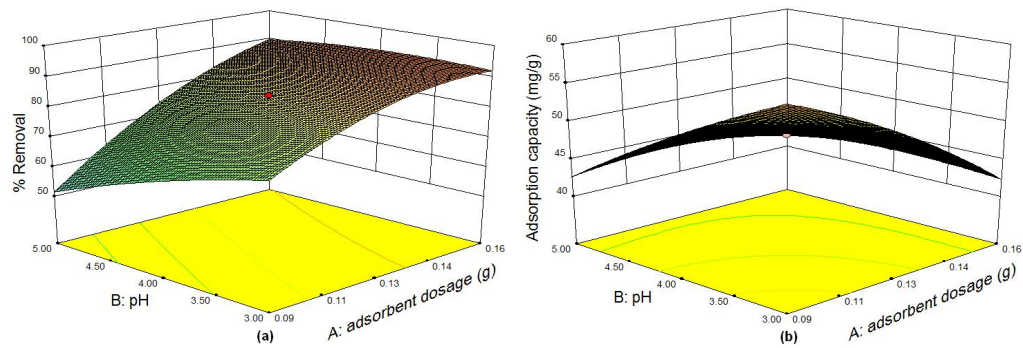


Fig. 9. The combined effect of pH and adsorbent dosage on (a) percentage removal and (b) adsorption capacity of SDCCB

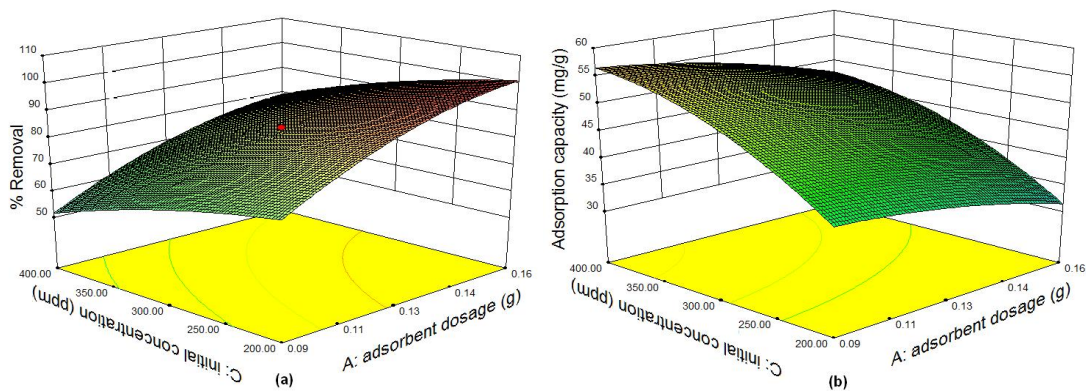


Fig. 10. The combined effect of initial concentration and adsorbent dosage on (a) percentage removal and (b) adsorption capacity of SDCCB

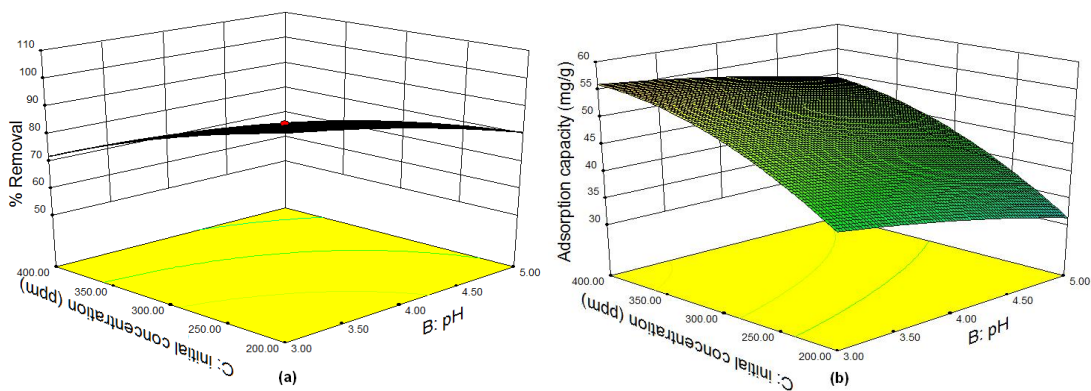


Fig. 11. The combined effect of initial concentration and pH on (a) percentage removal and (b) adsorption capacity of SDCCB

4. CONCLUSION

SDCCB is an effective, economic and eco-friendly adsorbent for the removal of 95% of Cr(VI) from aqueous solutions. The isotherm models for the experimental data followed is in the order of Freundlich > Langmuir > Temkin

isotherm for adsorption of Cr(VI) ions and adsorption kinetics was found to fit suitably in a pseudo second order kinetic model. The activation parameters evaluated points out that the adsorption of Cr(VI) on SDCCB surface is an endothermic chemisorption process. The mathematical model development and

optimization for adsorption of Cr(VI) using statistical design of experiments appears to be a useful tool to predict and understanding the interaction effects between process variables using CCD with RSM.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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