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OPTIMIZATION AND COLUMN STUDY ON HEXAVALENT CHROMIUM REMOVAL USING HYDROXYAPATITE BEADS DERIVED FROM MOSAMBI FRUIT PEEL

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ABSTRACT
This study elaborates on the preparation of hydroxyapatite particles from mosambi fruit peels by precipitation method. This hydroxyapatite was used as an adsorbent (AB) for the removal of *Cr (VI)* ion particles from wastewater. The adsorption was performed and optimized by desirability function to be pH 4, initial chromium concentration 200 mg/L, adsorbent dosage 0.425 g, and contact time 32.5 min, respectively using Response Surface Methodology (RSM). The Langmuir adsorption isotherm, pseudo-2nd-order, and Elovich model are well explained. Column experiments gave better results in the removal of *Cr (VI*) and this method is very effective for the treatment of industry effluent.
Keywords: Column Study, Optimization, RSM, Hydroxyapatite, Cr (VI), Mosmbi Peel.
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INTRODUCTION

The increasing population globally increasing food waste and the utilization of this waste is necessary due to serious environmental issues. The value-addition of utilizing this food waste will reduce not only the ecological burden but also help reduce the final cost of the end-products from food process industries. Food process industries focusing especially on fruit juices have ample amounts of waste in the form of peels, seeds, fibrous material, etc. There is growing interest in utilizing these waste peels and seeds of fruits, by extracting bioactive or using them as adsorbents for wastewater treatments. Chemical analysis reveals that certain wastes share similarities in composition with natural raw materials, often containing materials that are not only environmentally friendly but also beneficial for ceramic production.[1,2], adsorbents for toxin contained water treatment[3], and the bone material[4,5], nanoparticle synthesis[6] etc. Numerous researches have been undertaken to identify the natural AB from waste material and many techniques are available to synthesize these adsorbents. To name a few, the thermal methods or acid treatment[7,8] hydrothermal[9], solid-state reaction[10], chemical precipitation[11], radio frequency thermal plasma[12], and polymer-assisted synthesis method[13], are used for the synthesis of hydroxyapatite (HAP). Many of the researcher's extracted pectin from the different fruit peel (Citrus limonum) and it is used for the synthesis of nano HAP.[14] Heavy metals are highly toxic and heap up at diverse trophic levels *via* the nutrition chain and maltreatment the living beings. These produce perilous bugs or may damage the living body system. Therefore, it is vital to abate the discharge of these metals into the ether.[15,16] Different methods, like photocatalysis, membrane separation, biological oxidation, ozonation, adsorption (AP), ion exchange, oxidation, reverse osmosis, electro-dialysis, and electrochemical methodologies, have been used to eliminate trace metals from contaminated water.[17-21] The most frequently used AB is activated carbon. Raw and modified materials have been used for the elimination of wastewater, including clay, Ca-alginate hydrogel beads[22], guar gum-based hydrogels[23], wheat bran[24,25], walnut shell[26], fly ash, microalga Spirulina platensis[27], rice straw[28], cucumber peel[29], agricultural waste material[30], corncob, palm ash[31], Hordeum vulgare husk[32], Weeping Willow leaves powder[33], nanomaterials[34,35], and polymer particles.[36] Agronomic wastes are commonly used for WW treatment.[37] The hexavalent form *(i.e. Cr (VI))* is one of the unwanted heavy metals that cause different diseases.[38-40] In current eras, the AP process gaining more

challenge in the treatment of effluent because of its easy operation and low cost. The objective of this study is to prepare hydroxyapatite using mosambi peal (HAP-MP) and sodium alginate beads (SAB) using HAP-MP for *Cr (VI)* removal. The experiments were conducted in batch and continuous mode. Further modeling and kinetics studies were done for a better fit of the model.

EXPERIMENTAL

Materials and Methods

In this section, the details of the preparation of adsorbent HAP-MP and SAB using the HAP-MP procedure are depicted.

Preparation of HAP-MP and HAP-MP SAB

In the first stage, the hydroxyapatite (HAP) particles were prepared from mosambi peels (MP) using the method depicted by Nayar *et. al.*[41] and the detailed procedure discussed in Fig.-1. And stages of HAP-MP preparation are depicted in Fig.-2.

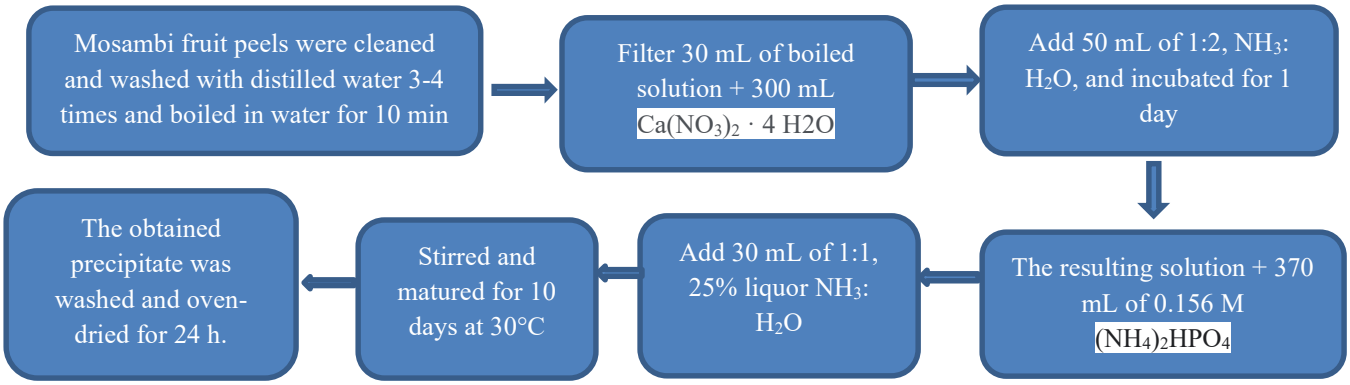


Fig.-1: Process Flow Sheet of Preparation of HAP-MP

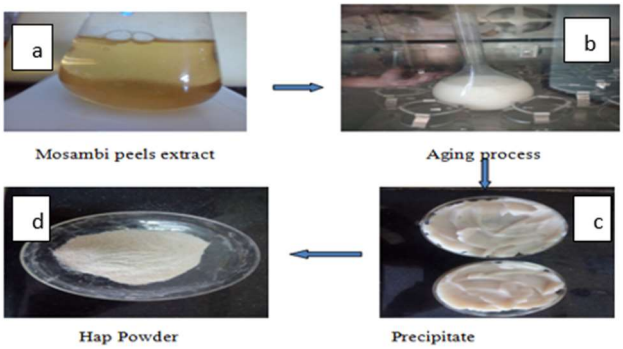


Fig.-2: HAP-MP preparation stages (a) Mosambi Peels Extract, (b) Aging Process, (c) Precipitate and (d) HAP

Further, in the next stage, HAP-MP powder will be used to prepare the alginate beads presented in Fig.-3. To achieve this, a solution of $NaC_6H_7O_6$ [AX] was prepared by liquefying 2 g of [AX] in 100 mL of distilled H_2O and keeping it for 20 min. The solution was slightly heated with constant stirring. A 1.0 g of HAP-MP was weighed and stirred with the sodium alginate solution for 45 min to form a homogeneous solution (Solution A). A 10 % $CaCl_2$ was prepared by dissolving 10 g of $CaCl_2$ in 250 mL of purified H_2O (solution B). Solution A was added drop by drop to solution B using a 20 mL syringe and was allowed to stand for 12 h to make the beads rigid. After 12 h, the excess water was decanted, and the stiff alginate beads were washed 2-3 times with sanitized water. The beads were stored in air-tight glass bottles till further use.

Batch Adsorption Study

The batch study was conducted using the IS 3052 standard. Figure-4 depicts the detailed process steps of the batch AP study.

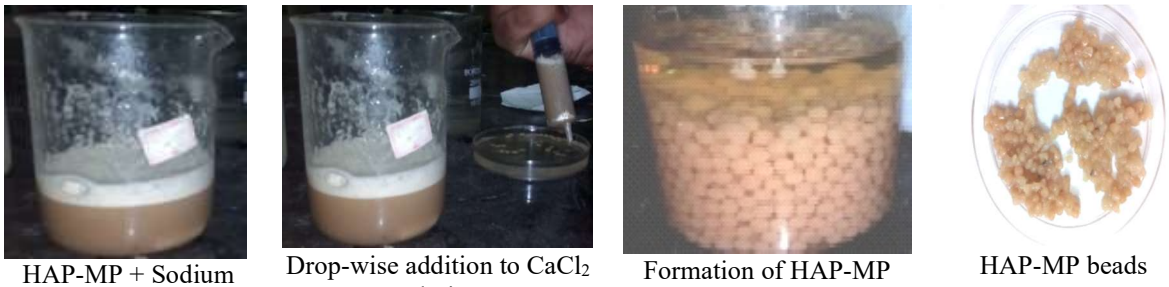


Fig.-3: Preparation of HAP-MP Alginate Beads

Fig.-4: Steps Involved in Batch Study for Cr (VI) Removal

Column Adsorption Study

This study is applicable for the constant purging of impurities from effluent, as this method has plenty of leads over the batch process. In the current study, the experiments were carried out using an acrylic column with an elevation of 50 cm. The HAP-MP beads were filled in the column and the synthetic wastewater was impelled from the lowest through the bed using a roller pump at a constant flow rate (FR) as shown in Fig. -5. The treated solution was collected at sporadic intervals from the set-up and the residual Cr concentration was calculated. Column specifications are listed in Table-1.

Table-1: Specifications of Packed Column

Parameters	Details
Bed length of AB	10 and 20 cm
Column diameter	4.0 cm
Area of the column	12.56 m^2
Weight of AB taken	45 g
The volume of the aqueous solution taken	2000 litre
FR	3-, 5-, and 7-mL min^{-1}

Optimization Study

In this section, the 4 parameters i.e. *Cr (VI)* initial concentration (IC) (50 – 200 mg/L), pH (2 - 8), adsorbent dose (AD) (0.05 to 1 g/100 mL), and contact time (CT) (5 – 120 min) at additional levels with a marginal number of experiments suggested by CCD.[42] Design Expert software (DES) 9.0.3.1 was employed for optimizing the AP process. The design featuring three levels - low, medium, and high - was encoded as -1, 0, and +1, the details listed in Table-2. The results underwent analysis using both 3D plots and analysis of variance (ANOVA).[43,44]

Redevelopment of the Spent Adsorbent

This methodology is a crucial part takes an economic and eco-friendly point of view. Figure-6 displays the procedure for the regeneration of beads.[46]

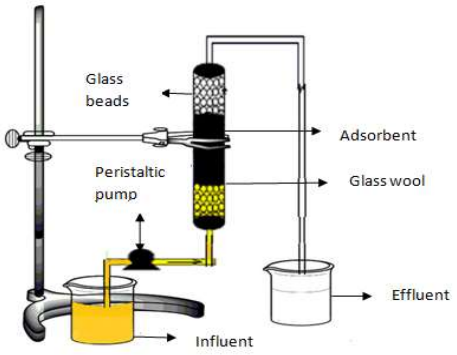


Fig.-5: Schematic of the Experimental Setup of Continuous Column Adsorption

Table-2: Experimental factors and levels for the CCD

Factor	-1	0	+1
IC, ppm	50	125	200
AD, g/100 mL	0.05	0.5	1.0
pH	2	5	7
CT, min	5	30	60

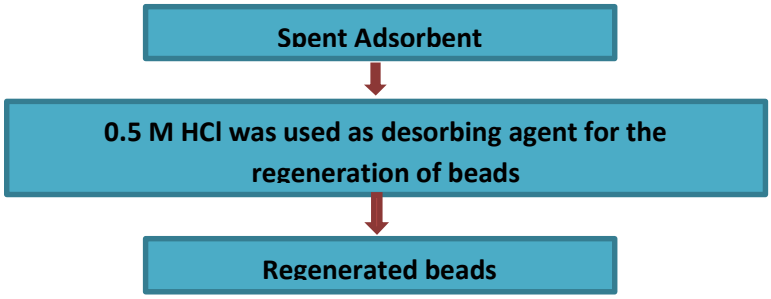


Fig.-6: Preparation of Regenerating Beads

RESULTS AND DISCUSSION

Characterization of HAP-MP

The physicochemical properties of HAP-MP adsorbent were analyzed and those are listed in Table-3.

Table-3: Properties of HAP-MP

Parameters	Details
Specific gravity	0.002
BET surface area, m^2/g	87.1779
Particle size, nm	34.378
Bulk density g/cm^3	2.00
Pore volume, cm^3/g	0.046441
Pore diameter, Å	21.309

XRD Studies

The main summits related to HAP were witnessed at 2θ values of 25°, 29°, 32°, 40°, and 50° shown in Fig.-7. The outcomes matched with JCPDS no. 09-0432, which inveterate the establishment of HAP from MP. Analogous fallouts have been confirmed by Nayar. [41]

FT-IR Studies

Figure-8. shows the wide band perceived around 3402.4 cm^{-1}, 3410 cm^{-1}, and 3578 cm^{-1}, equivalent annotations have been reported by Fu *et al.* and Li *et al.* [47,48] The sharp peak at 594.93 cm^{-1}signifies the

vibration peaks of the PO_4^{3-} group. The peak saw at 1376.2 $cm^{-1}$is assigned to CO_3.[2- 49,50] The peaks at 1134.4 cm^{-1} and 861 cm^{-1} indicate the interaction of CO_2 with the AB and broadening mode of the PO_4^{3-} group. [51] The peaks at 1989.33 $cm^{-1}$and 1376.2 cm^{-1} are due to C-H bending. The change in peaks at 2246.9 $cm^{-1}$to 2073.3 $cm^{-1}$and 2111.4 $cm^{-1}$to 1989.33 cm^{-1} may be due to O=C=O stretching and AP of Cr (VI) onto HAP-MP. There is no transformation in the summits at 1134.4 cm^{-1} (before) and 1622 cm^{-1} (after) AP of *Cr (VI).*

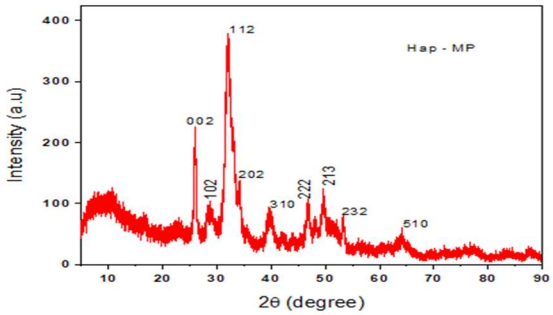


Fig.-7: HAP – MP XRD Pattern

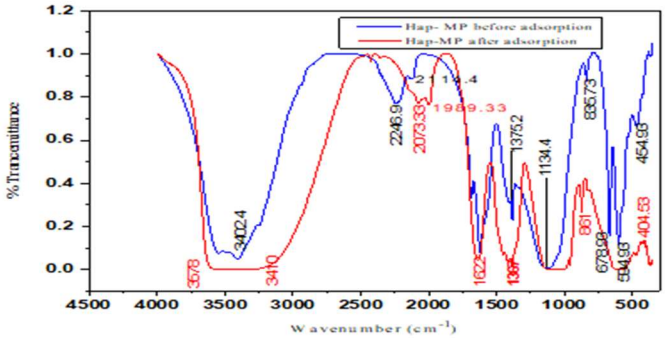


Fig.-8: FT-IR of HAP - MP (-) before and (-) after Adsorption of Cr (VI)

SEM and EDS Studies

The existence of Ca and P in HAP-MP helps in the size and surface structure of HAP particles. These SEM images discovered the bunches-like structure depicted in Fig.-9a; the size of particles ranges from 5 – 20 nm. This may be because of (90 – 95%) of limonene content. And same kind of data was witnessed by Dharmawan *et al.* [52] After *Cr (VI)* AP the images are exposed in Fig.-9b. Thus, it shows the shallowness of the AB attached with a small number of particles of and spike-like shape onto the material after AP whereas it is lacking in the SEM images of Fig.-9a.The study specifies the presence of Ca (43.43%), and P (18.65%) before AP Fig.-10a, while after the AP of *Cr (VI),* these Ca and P elements percentage reduced, and Cr (5.20%) was found same displayed in Fig.-10b. This is because of may be due to the interaction with the *Cr (VI)* ion during the AP process.

Experimental Design and Data Analysis

The CCD was used to determine the outcome of the factors as displayed in Table-2. The experimental design created by the DES is illustrated in Table-4.

Table-4: DES for HAP-MP

A: pH	B:AD (g/100mL)	C: CT (min)	D: IC mg/L	% AP	Predicted value
6	0.425	32.5	125	64.2	64.35
4	0.425	32.5	125	68.51	67.72
4	0.8	32.5	125	70.2	70.66
4	0.425	60	125	68.4	68.22
2	0.05	60	200	78.21	79.10

6	0.8	60	200	81.33	81.78
2	0.8	5	200	83.9	84.91
2	0.425	32.5	125	69.25	69.64
2	0.05	60	50	54.5	54.49
4	0.05	32.5	125	62.91	62.98
6	0.05	60	50	50.12	49.72
4	0.425	5	125	65.34	66.06
4	0.425	32.5	50	54.54	57.29
4	0.425	32.5	125	68.99	67.72
6	0.8	5	200	79.83	79.10
4	0.425	32.5	125	67.56	67.72
6	0.8	5	50	55.24	54.96
4	0.425	32.5	125	66.55	67.72
6	0.8	60	50	56.52	56.91
4	0.425	32.5	125	68.12	67.72
2	0.8	60	200	86.97	87.25
2	0.05	5	200	77.88	76.74
2	0.8	5	50	61.58	61.13
4	0.425	32.5	125	68.23	67.72
6	0.05	60	200	75	74.70
2	0.05	5	50	52.7	52.86
4	0.425	32.5	200	83.87	81.66
6	0.05	5	200	70.25	71.99
2	0.8	60	50	63.88	62.75
6	0.05	5	50	48.77	47.74

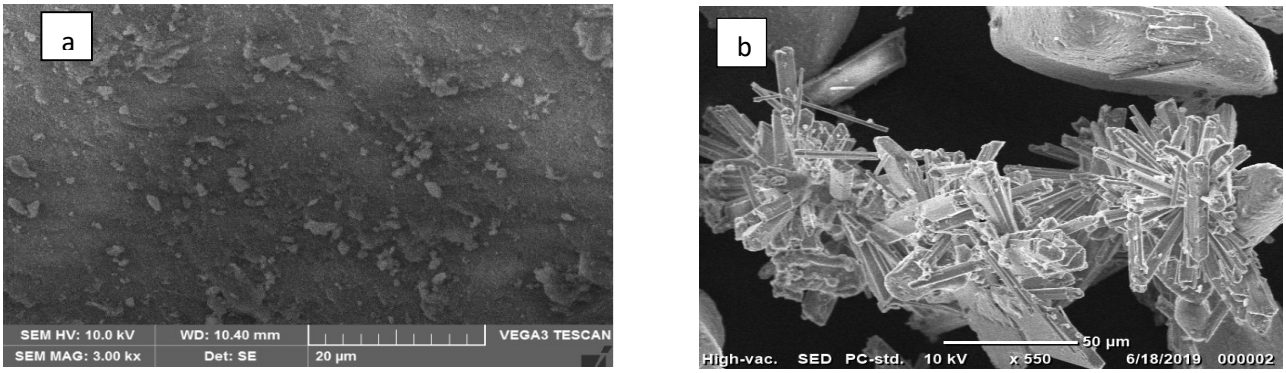
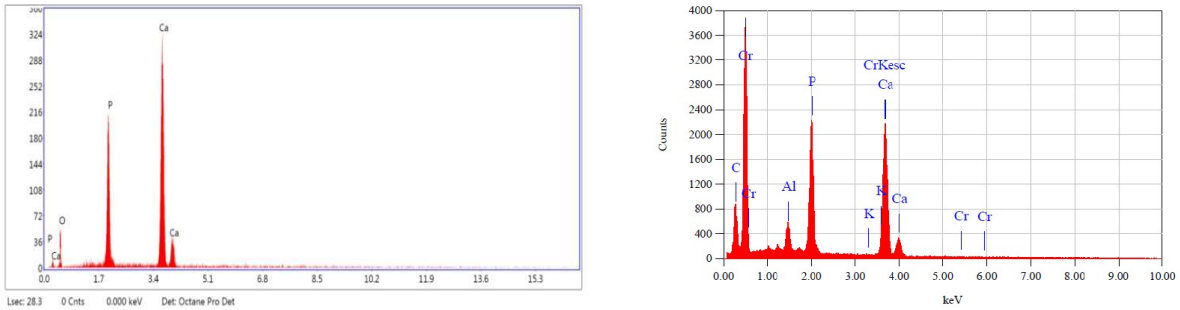


Fig.-9: SEM Images of HAP - MP (a) before and (b) after AP



(a) (b)

Fig.-10: EDS Analysis of HAP-MP (a) before and (b) after AP

Finally, the lack of fit and model was verified for significance based on the p-value and the conversion with the ultimate R^2 value. Table-5 symbolizes the ANOVA for the response of the *Cr (VI)*.

Table-5: ANOVA Results for HAP-MP

Source	Sum of squares	Degree of freedom (df)	Mean square	F-value	p-value (prob > F)	Significance
Model	3098.82	14	221.34	121.11	< 0.0001	Significant
A-pH	125.93	1	125.93	68.90	< 0.0001	Significant
B-AD	265.34	1	265.34	145.19	< 0.0001	Significant
C-CT	21.00	1	21.00	11.49	0.0040	Significant
D-IC	2674.00	1	2674.00	1463.13	< 0.0001	Significant
AB	1.13		1.13	0.62	0.4431	
AC	0.12		0.12	0.065	0.8020	
AD	0.13		0.13	0.073	0.7908	
BC	4.0×10^{-4}		4.0×10^{-4}	2.189×10^{-4}	0.9884	
BD	0.012		0.012	6.6×10^{-3}	0.9362	
CD	0.53		0.53	0.29	0.5971	
A^2	1.38		1.38	0.76	0.3984	
B^2	2.10		2.10	1.15	0.3008	
C^2	0.89		0.89	0.49	0.4967	
D^2	7.93		7.93	4.34	0.0547	
Residual	27.41	15	1.83			
Lack of Fit	23.81	10	2.38	3.30	0.0996	not significant
Pure Error	3.60	5	0.72			
Corrected Total	3126.23	29	R-Squared	0.9912	Adj R-Squared	0.9830
Std. Deviation	1.35		Pred R-Squared	0.9548	Adeq Precision	41.327
Mean	67.45	C.V %	2.00			

The F value and p-value evidence the importance of the suggested model. In this case, by noting all data in Table-5 confirms that the model fits the obtained data. This model is said to be adequate. Figure-11 shows the 3-D response surface plots for *Cr (VI)* AP.

Equilibrium Studies

Studies were carried out in 250-mL Erlenmeyer flasks on 100 mL of solution containing IC as 100 ppm. The AD was varied with known mass. The pH was adjusted to 4. These flasks were agitated at 120 RPM and maintained at 30^0C for 4 h. The solutions were filtered and analyzed.

Isothermal Analysis

The R^2 value of the Langmuir AP isotherm for HAP-MP (0.993) was established to be superior to those for the other isotherms shown in Fig.-12.

The slope (n=0.03) value of the isotherm satisfies the condition $0 < n < 1$.[53] The best fit of the Langmuir isotherm with a high R^2 value specifies the creation of a single layer on the outer surface of the AB.[54] In this case, the R_L (0.27) value is between 0 and 1indicating that the AP is favourable. The R^2 values Temkin plot were moderately low ($R^2 = 0.54$) and it is not a good fit.

Adsorption Kinetics

The pseudo-2nd-order (PSO) kinetic model gave the highest R^2 value for HAP-MP as given in Fig.-13. These values were found to be greater than those obtained for the other models. Thus we can conclude that the AP process obeys the PSO model. The highest AP ability was found to be 8.76 $mg.g^{-1}$ for HAP-MP. In the current study, for the intraparticle diffusion model, the AB showed ($R^2 = 0.982$) values for HAP-MP and are linear, but do not pass through the origin, which leads to the diffusion mechanism being involved in the sorption processes, and may the rate-determining step.[55-57]

The Elovich equation describes chemical AP in nature. In this study, the plots fulfil the necessary criteria, with ($R^2 > 0.9$), suggesting that diffusional rate-limiting may be more significant.[58] Hence this model also fits the data.

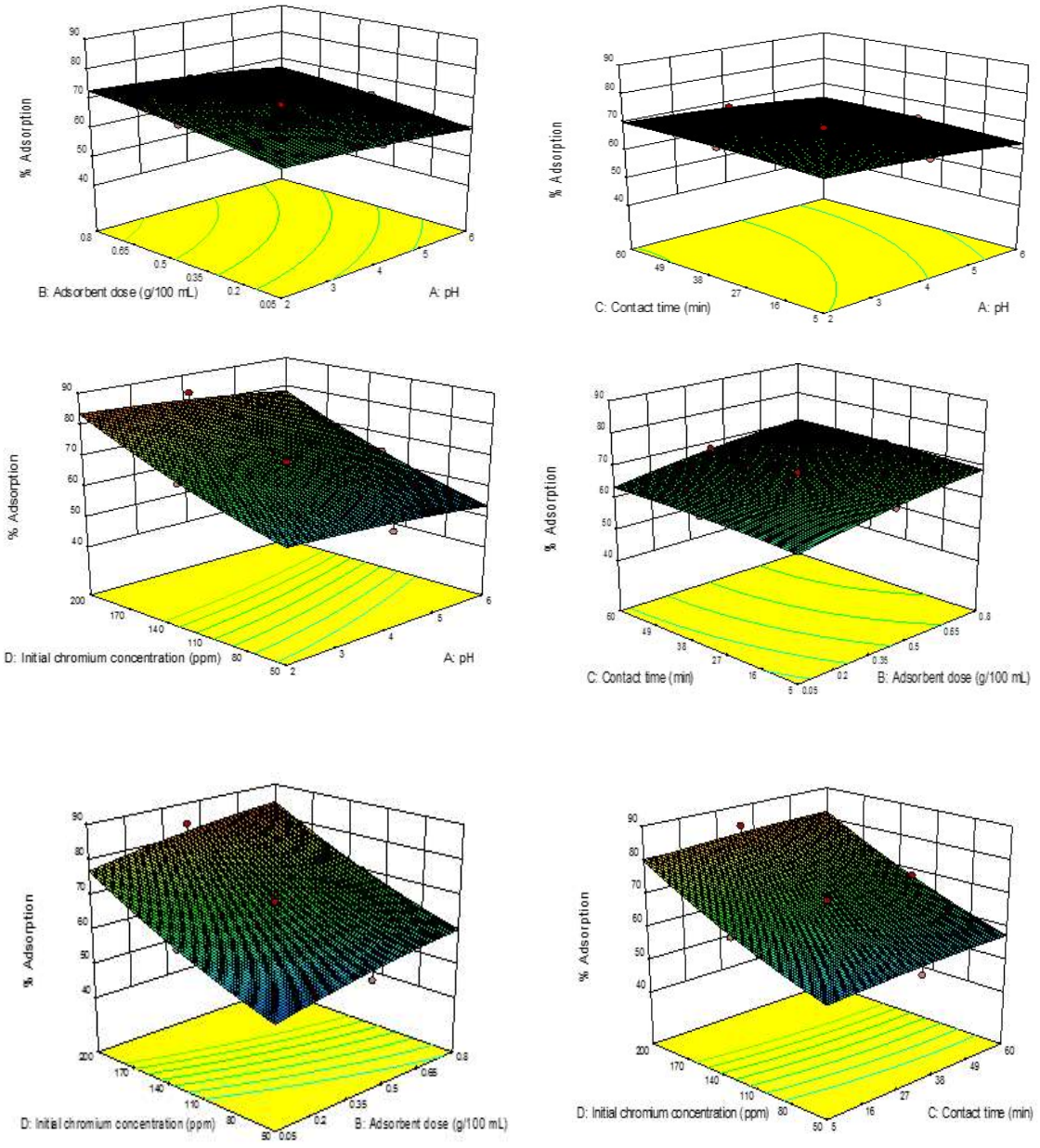


Fig.-11: 3-D Plots of Cr (VI) Adsorption by HAP - MP

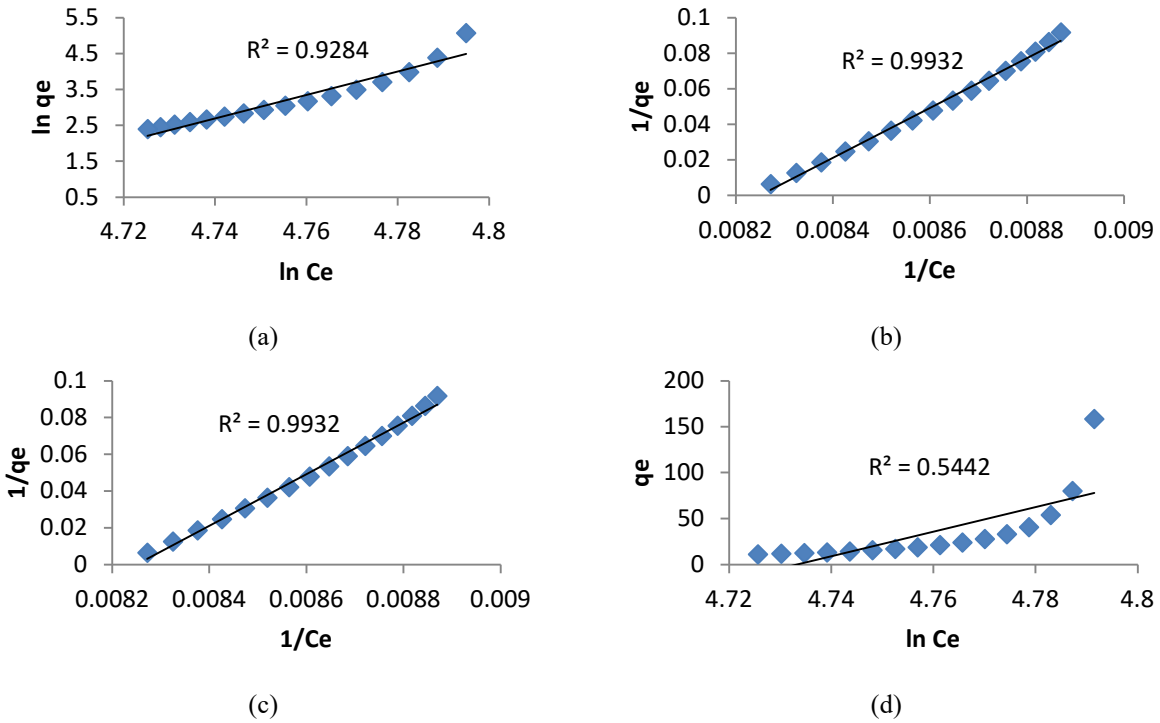


Fig.-12: Isotherm Plots (a) Freundlich, (b) Langmuir, (c) D-R, and (d) Temkin Isotherms for the Adsorption of *Cr (VI)* by HAP – MP

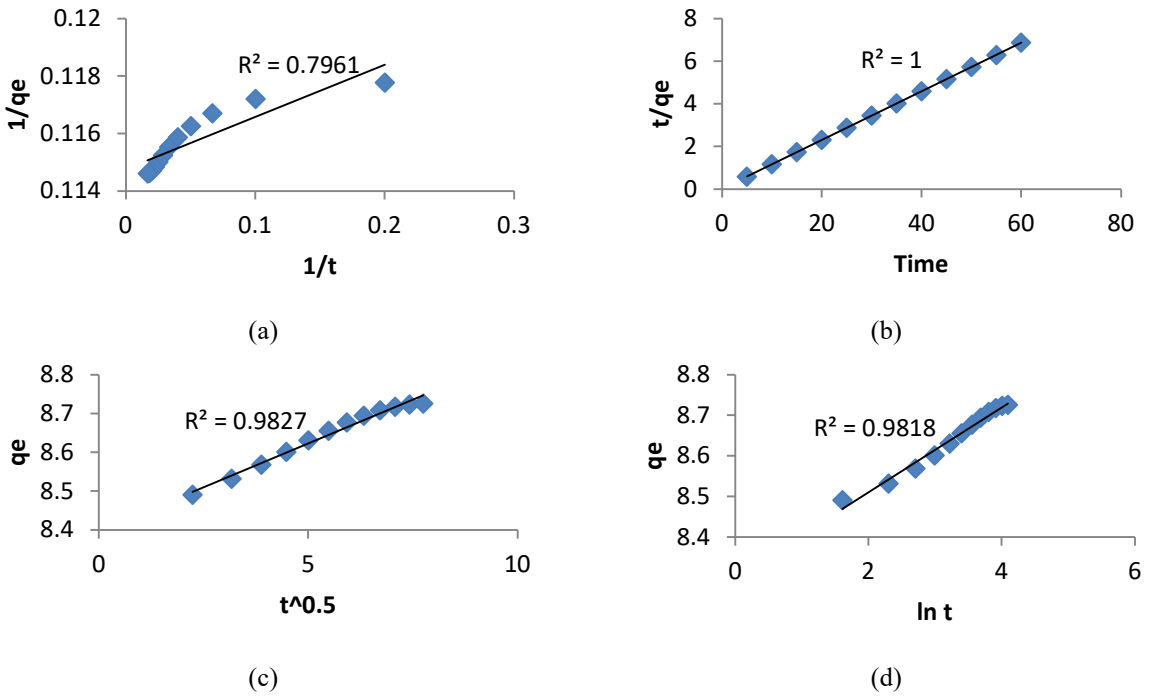


Fig.-13: Kinetic Studies on HAP-MP (a) First-Order, (b) PSO, (c) Intraparticle Diffusion, and (d) Elovich Model

Column Study: Impact of Initial Cr (VI) Concentration

The influence of Cr (VI) IC (50 mg/L and 200 mg/L) on the column's performance at a flow rate of 3 mL/min and a bed height (BH) of 20 cm is illustrated in Fig.-14. In this breakthrough exhaustion time (BT and ET) dropped at high Cr concentration. The lower *Cr (VI)* level in the influent (50 mg/L) the level of *Cr (VI)* removal (%) significantly increased to 69.9%. Breakthrough curve (BC) parameters are listed in Table -6.

Table-6: Parameters of BC

Co, mg/L	Q, mL/min	Bed height	t_b	t_e	%R
50	3	20	180	660	69.69
100			30	285	59.64
150			30	195	37.6
200			30	165	30.3

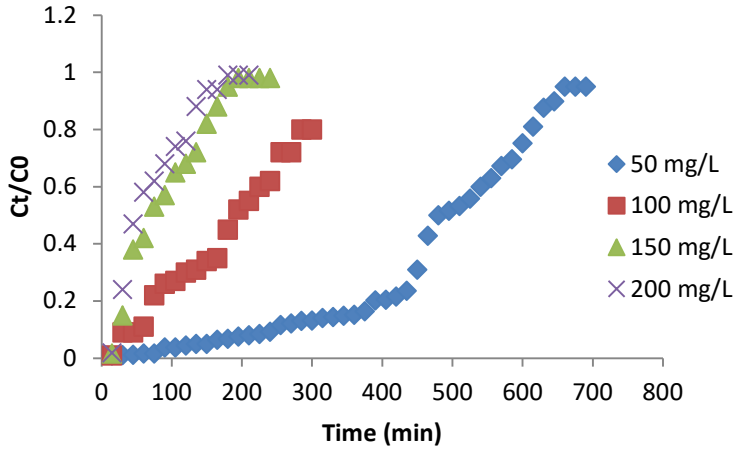


Fig.-14: Breakthrough Curves for IC

Effect of Bed Height

Two beds of 10 and 20 cm in height containing 15 and 25 g of the AB were used for the experiment. A 50 mg/L IC was used at a FR of 3 mL/min. The BC for AP of the *Cr (VI)* on selected BH is shown in Fig.-15.

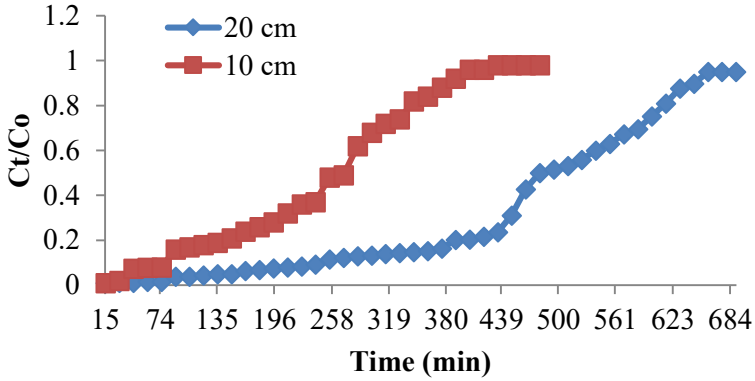


Fig.-15: Breakthrough Curve for BH

The BT and ET are found to rise with the rise in BH. It can be ascribed to the rise in sorption cited and the interaction period due to the huge quantity of AB vacant in the column.[59,60] An increased BT was obtained with higher BH also it produced an increase in the ET. Nguyen *et al.*[61] reported analogous remarks. Increasing the BH and by keeping the feed concentration constant leads to a larger surface area with more active sites on the adsorbent's surface, resulting in improved AP.[62] Moreover, as the BH increases, the diffusion process becomes more significant in mass transfer and decreases axial dispersion. This allows Cr (VI) ions more time to diffuse into the AB.[63]

Effect of Flow Rate

Studying the impact of FR is significant as it is a crucial parameter in designing an adsorber. The adsorbent's sorption capacity data for Cr (VI) ions solution with an IC of 50 mg/L at a BH of 20 cm is examined and presented for FR of 3,5 and 7 mL/min in Fig.-16.

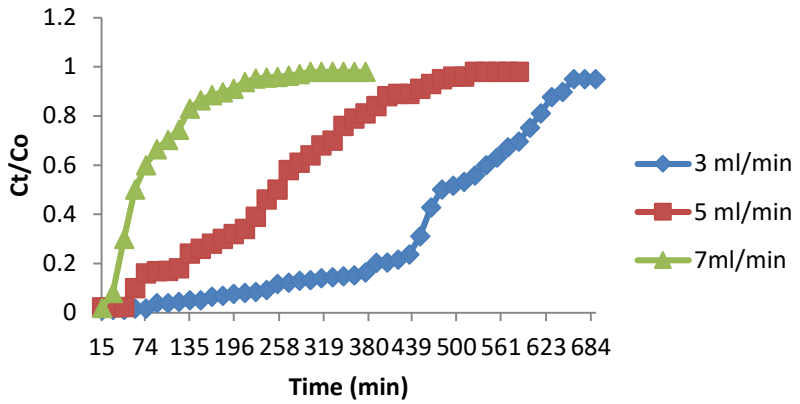


Fig.-16: BC for Different Flow Rates

As the FR is improved, the BC becomes steeper and reaches the breakthrough point quickly. Details of parameters for the effect of different FR on 20 cm BH are displayed in Table-7. At higher FR, the CT among the adsorbate and AB are reduced; foremost to a timely BT.[64] The uptake of *Cr (VI)* for the 20 cm column was found to be 69.69 %.

Table-7: Parameters Impact of FR on 20 cm BH

Q, ml/min	t_b	t_e	%R
3	80	280	69.69
5	60	525	27.42
7	30	300	21.21

Yoon Nelson Model

This model can predict the duration for a 50% adsorbate breakthrough.[65] The Fig.-17 (a) shows the Yoon–Nelson model plot with ($R^2 = 0.98$), and the model gave an exceptional apt to the obtained data. In this, a τ (min) -1.84, value indicates that more adsorbate can be bound by an exact AB.

Thomas Model

In this model k_{Th} (mlit/min mg) is the Thomas model constant, and q_0 (mg/g) is the AP capacity. The k_{Th} and q_0 can be found from the line plot of $\ln[(C_0/C_t) - 1]$ against t and displayed in Fig.-17 (b). The maximum value of k_{th} was observed at $q_0 = 5.13$ mg/g corresponding to $R^2 = 0.98$, signifying that this model ensued a good fit to the obtained value.

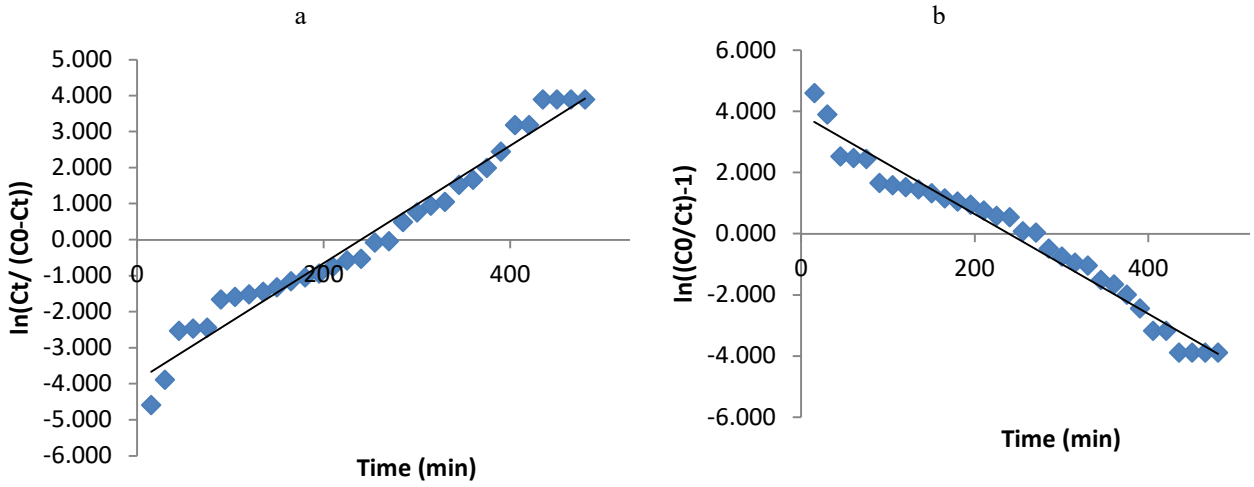


Fig.-17: Linear Plots of (a) Yoon–Nelson Model (b) Thomas Model for SAB at IC: 50 mg/L, FR: 3 mL/min, and BH: 20 cm

CONCLUSION

The HAP-MP was confirmed by the characterization techniques. The optimal conditions for the AP of *Cr (VI)* onto HAP-MP are IC of Cr (VI) is 200 ($mg.L^{-1}$), AD 0.425, pH of 4, contact time of 32.5 and removal efficiency is 83.87%. The 3D plots explicate the combined effects of all the parameters on the AP process. ANOVA models were significant to the experimental data. The obtained data fitted well with the Langmuir isotherm, pseudo-2nd-order, and Elovich models. Thus, it can be concluded that HAP-MP is good and recyclable AB. From the column studies it is observed that the increase in the metal uptake capacity with the rise of BH is due to the increase in the contact time. Greater FR (3, 5, and 7 mL/min) led to increased highest q_0 but declined *Cr (VI)* removal. The Thomas and Yoon–Nelson kinetic AP models delivered a positive good match to the *Cr (VI)* AP. The desorption experiments with 0.5 M NaCl showed good performance over the first 2 cycles, whereas a decline was evident for 3rd cycles.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All authors significantly contributed to this manuscript, participated in reviewing and editing, and approved the final draft for publication. The authors' research profiles can be verified through their ORCID IDs listed below:

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