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ORIGINAL ARTICLE

Response surface methodology as a statistical tool for optimization of removal of chromium (VI) from aqueous solution by Teff (*Eragrostis teff*) husk activated carbon

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Abstract
Recently, rapid industrialization leads to excessive release of heavy metals such as Cr(VI) in the environment. Exposure to chromium (VI) can cause kidney and liver damage, depressed immune systems, and a variety of cancers. Therefore, treatment of Cr(VI) containing wastewater is mandatory. This study aims to optimize the removal of Cr(VI) from aqueous solution using locally available Teff husk activated carbon adsorbent. The laboratory-based study was conducted on the optimization of Cr(VI) removal efficiency of Teff husk activated carbon from aqueous solution. A central composite design was used to examine the effect of the interaction of process parameters and to optimize the process using Design Expert version 7.0 software. The optimized removal efficiency of Teff husk activated carbon (95.597%) was achieved at 1.92 pH, 87.83 mg/L initial concentration, 20.22 g/L adsorbent dose, and 2.07 H contact time. The adsorption of Cr(VI) on Teff husk activated carbon was found to be best fitted with pseudo-second-order kinetics and Langmuir isotherm model of the adsorption. Teff husk activated carbon can be used as an efficient adsorbent for removal of chromium (VI) from contaminated water. Column adsorption needs to be studied in the future.

Keywords Batch adsorption · Chromium (VI) · Teff husk activated carbon · Central composite design

Introduction

The generation rate of wastewater is increasing dramatically worldwide due to the increased consumption of water. Globally, over 80% of the wastewater is discharged to the environment without prior treatment (UN-WWAP 2017). The problem is severe in developing countries because they discharge more than 90% of the wastewater into the environment without proper treatment. In the 21st century, the rapid industrialization leads to excessive release of heavy metals into the environment, which has a significant adverse effect on human health and the environment (Sato et al. 2013). Recently, chromium pollution is a heavy metal pollution that has been a major focus of researchers (Renuga et al. 2010). Chromium may be found as Cr(III) and Cr(VI) in industrial wastewater (Mullick et al. 2017). Its hexavalent form has gotten a great concern due to its hazardous property and carcinogenic to exposed peoples (Renuga et al. 2010; Zhang et al. 2012).

Cr(VI) adversely affects the kidney and liver and causes dermatitis, diarrhea, mouth ulcers, nosebleeds, low white blood cell counts—hence depressed immune defense systems, miscarriages, and a variety of cancers (Solomon 2008; Singh and Singh 2012). According to the Blacksmith Institute's world worst pollution problems, chromium pollution adversely affects about 16 million people in 2015 globally (Black-Smith-Institute 2015). In aquatic ecosystems, chromium is known to bioaccumulate in algae, aquatic plants, invertebrates, and fish. Toxicological studies proved that hexavalent chromium, even at relatively low concentrations, can cause reduced growth and photosynthesis in algae and

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aquatic plants; and lethal toxicity, behavior changes; and decreased growth, reproduction and survival in invertebrates; and changes in physical and bio-chemical conditions, increased hatching time, DNA damage, and reduced survival in fish (MiningWatch 2012). For instance, 62 ppb of Cr(VI) inhibits growth in algae and 16 ppb inhibits growth in fish (Solomon 2008).

In Ethiopia, currently there are more than 30 tannery industries in operation. Most of the Ethiopian leather industry uses chrome tanning and discharges their wastewater to nearby water bodies without adequate treatment. As a result, it adversely affects the aquatic ecosystem and the community around the river that uses the water bodies for drinking, personal hygiene, irrigation, etc. The effluent concentration of Cr(VI) in most of the industries in Ethiopia is in the range of 28–45 mg/l (Birhanie et al. 2017), which is much greater than the WHO and Ethiopian Environmental Protection Authority (EEPA) standard value of 0.1 mg/l (Kebede and Gashaw 2016). In view of the pollution hazard caused by Cr(VI), treatment of wastewater to remove excess chromium is imperative.

Several technologies have been applied to remove Cr(VI) from aqueous solutions including precipitation, reverse osmosis, ion exchange, filtration, sand filtration, chemical reduction/oxidation, electrochemical precipitation, membrane filtration, solvent extraction, and electrochemical deposition. However, all of these techniques suffer from various limitations including incomplete metal removal, high reagent consumption and energy utilization, low selectivity, and generation of secondary wastes that are difficult to dispose off (Tesfaye 2016; Azimi et al. 2017; Aravind et al. 2016). Thus, adsorption is the best suited method that can be used in low income countries like Ethiopia due to its inexpensiveness and efficient removal of heavy metals. Due to its high-porosity, activated carbon (AC) is one of the most commonly used alternatives for the removal of Cr(VI) from drinking and wastewater (Zhang et al. 2012). Therefore, it is important to find a way to remove hexavalent chromium using inexpensive adsorbents.

In the present study, an activated carbon that is produced from Teff husk, an agricultural solid waste obtainable from Teff (*Eragrostis Teff*), was utilized for the removal of Cr(VI) from aqueous samples. Teff (*E. Teff*), a cereal crop that belongs to the grass family *Poaceae*, is endemic to Ethiopia. It is the most common and native cereal crop mainly produced in Ethiopia with the largest share of cultivation, over 2.8 million hectares (25–30%) (Kibatu et al. 2017). It is primarily cultivated for its grain for human consumption and its straw and husk for livestock forage. It is also cultivated in most of the country especially in the highlands and able to grow under a wide range of ecological conditions such as on waterlogged area to drought environments. Teff husk is abundant, locally available, and low-cost agro-waste in Ethiopia (Vandercasteelen et al. 2013; Stallknecht et al. 1993; Gebretsadik et al. 2009). Therefore, Teff husk can be used as a potential precursor for the production of low cost activated carbon. No research has been done on the optimized application of THAC for removal of Cr(VI) from an aqueous solution. The purpose of this research is to optimize the efficiency of low-cost, locally available Teff (*E. Teff*) husk activated carbon for removal of chromium (VI) from aqueous solution.

Methods and materials

Experimental design

A laboratory-based experimental study was conducted at the University of Gondar from March to June 2018 Gondar, Ethiopia.

Chemical and reagents

All chemical and reagents in this study were analytical grade (> 99% pure). Working Cr(VI) solutions were prepared from the stock solution (1000 mg/L) by successive dilutions using distilled water. The sample solution pH was adjusted by adding drops of either NaOH or HCl (1 M each) solution whenever required.

Preparation of the Teff husk activated carbon

The Teff husk was collected from the farmers around Gondar using pre-cleaned polyethylene bags. The Teff husk sample was washed with distilled water and sun dried; followed by oven dried at 105 °C for 24 h to remove the excess moisture. The dried sample was mixed with 1:3 w/w % of conc. H_2SO_4 and kept at room temperature for 24 h. Then, the solid residue was washed with distilled water and neutralized by soaking in 2% $NaHCO_3$ solution for a day. The product was also air-dried at room temperature and kept in hot air oven at 120 °C for 10 h and then transferred to a muffle furnace kept at 550 °C for an hour (Yimer et al. 2014). Finally, the dried activated carbon was crashed and powdered into a sieve size of 1–2 mm and preserved in desiccators for further use (Tesfaye 2016).

Characterization study of Teff husk activated carbon

The Teff husk activated carbon was characterized in terms of its physical and chemical characteristics (Table 1). American Society for Testing and Materials (ASTM international) standard methods for characterization of activated carbon have been used as described in Table 1. The presence of various functional groups present on the surface of the

Table 1 Standard methods applied to measure characteristics of THAC

Characteristics of THAC	Standard methods used	References
Carbon yield		Emirie (2015)
Moisture content	ASTM D2867-99 method	ASTM (1999a)
Volatile matter	ASTM D5832-95 method	ASTM (2003)
Ash content	ASTM D2866-94 method	ASTM (2004b)
Fixed carbon		Emirie (2015)
Bulk density and porosity	ASTM D2854-96 method	ASTM (2004a)
Specific surface area	Sears method	Yimer et al. (2014)
P^H	ASTM D3838-80 method	ASTM (1999b)
Point of zero charge	Solid addition method	Emirie (2015)

adsorbent and their role in adsorption were also analyzed using FT-IR (Fourier transform infrared) spectrum within the range of 400–4000 cm^{-1} using FT-IR-65 Spectrometer.

Batch adsorption experiments

Effect of individual process parameters

Batch adsorption experiments were conducted to investigate the effect of pH, initial concentration of Cr(VI), adsorbent dose, and contact time on Cr(VI) removal efficiency of THAC (Emirie 2015; Dula et al. 2014; Kakavandi et al. 2014; Ali et al. 2016; Ali and Alrafai 2016). The range of each of the four process parameters was determined based on previous studies as stated in Table 2 and taking the others variables constant.

Flasks containing 100 ml of samples were agitated by using thermostatic shaker with 25 °C at 200 rpm for all experiments. Then, the samples were filtered by using Whatman No.1 filter papers, and supernatant was analyzed for Cr(VI) ion concentration by flame atomic absorption spectrometer. The blank adsorption experiments were also carried out. Then, the removal efficiency of THAC was determined (Tesfaye 2016).

$$\text{Removal Efficency }(\%) = \frac{C_o - C_t}{C_o} \times 100 \tag{1}$$

Where C_o and C_t are the Cr(VI) concentrations in mg/L initially and at a given time t, respectively.

Optimization of process parameters

The optimum adsorption conditions and the interaction of the four variables considered in this study were determined by response surface methodology (RSM) through face-centered central composite design (CCD) (Gnanasundaram et al. 2017). RSM is the best design to find the ideal process settings and achieve the optimal performance of a surface processes (Magoling and Macalalad 2017; Gnanasundaram et al. 2017). For each factors −1 and +1 levels were estimated from the batch experiment. Then 30 random runs generated by CCD and computed by the formula: $N=2^f+2f+f_c$, where f is the number of factors and f_c is the center runs, were tested. The adsorption process was conducted for each solution with three levels (−1, 0, +1) of pH, initial concentration of Cr(VI) ions, dose of activated carbon, and contact time as described in Table 4. Then, the Cr(VI) removal efficiency of THAC and its optimum condition have been determined. Design expert software version 7.0.0 was used for the modeling and optimization experiment.

Isotherm and kinetics studies

Adsorption isotherm was also studied with different initial concentration of Cr(VI) (100, 150, 200, 250 mg/L) and optimum pH, AC dose, and contact time. Then, equilibrium concentration (C_e), amount of adsorbed adsorbate at an equilibrium (q_e), and specific adsorption (C_e/q_e) were calculated to determine the isotherm of the adsorption. Then, the isotherm was examined whether it is fitted to Langmuir isotherm model by plotting (plot C_e/q_e vs C_e) (eq. 3) or Freundlich isotherm model (plot log q_e vs 1/log C_e) (eq. 4) using R-squared value (Tesfaye 2016).

Table 2 Ranges of process parameters at which adsorption test was conducted

Parameter to be examined	Range	References
pH	1, 2, 3, 4, 5, 6	Rai et al.(2016), Kebede and Gashaw (2016), Emirie (2015), and Berihun (2017)
Initial Cr(VI) conc. (mg/L)	50,100,150, 200, 250	TESHOME (2015) and Rai et al. (2016)
Adsorbent dose (gm)	0.5, 1, 1.5, 2, 2.5	Dula et al. (2014)
Contact time (h)	0.5, 1, 1.5, 2, 2.5	Berihun (2017) and Dula et al. (2014)

Adsorption kinetics was examined with batch adsorption by making conc. of Cr(VI), pH and, dose of AC at optimum condition with different the contact time (0.5, 1.0, 1.5, 2.0 h). Then, the amount of adsorbed adsorbate at an equilibrium (q_e) and amount of adsorbed adsorbate at any instant of time t (q_t) were calculated to determine the kinetics of the adsorption. Then, the adsorption kinetics was also tested whether it is fitted to pseudo-first order kinetics (plot log ($q_e - q_t$) vs t) (Eq. 5) or pseudo-second-order kinetic models (plot $1/q_t$ vs t) (Eq. 6) using R-squared value (Tesfaye 2016).

Statistical analysis and modeling of Cr(VI) adsorption

Design Expert (version 7.0.0) software was used for statistical data analysis. The analysis was carried out using the response surface methodology (RSM) through three level central composite design (CCD) (Emirie 2015). The statistical analysis that was performed includes model selection, model fitness test, and ANOVA analysis. A model was selected depending on p value, lack of fit, and R-squared values. The effect of each independent variables and their interactions on the response variable were evaluated by ANOVA. Log transformed second-order polynomial regression was also used to evaluate the magnitude and direction of the effect of individual process parameters [pH (A), initial concentration of Cr(VI) (B), adsorbent dose (C), and contact time (D)] and their interaction on the removal efficiency of THAC. R-squared value was also used to select the better fit isothermal and kinetics model of the adsorption.

Data quality control

The chemicals used in the study were standardized. The flame atomic absorption spectrometer (FAAS) was calibrated with seven standard solutions of Cr(VI) (0, 2, 4, 6, 8, 10, and 12 ppm). Then, the calibration curves were drawn (absorbance vs concentration of Cr(VI)), and the analysis of samples was performed when the R-squared is greater than 0.99 (Annex 1 in supplementary material).

Results and discussion

Characterization of the Teff husk activated carbon

The physicochemical characteristics of THAC (Table 3) show as the prepared activated carbon has good quality to be used as an adsorbent for removal of hexavalent chromium from aqueous solution. As clearly stated on Table 3, the prepared AC contains lower ash content, volatile matter, and moisture content as compared to some of the activated carbons produced from different

Table 3 Comparison of characteristics of the prepared activated carbon

AC	Activation method	Characteristics of activated carbon										References
		CY %	FC (%)	MC (%)	AC (%)	VM (%)	Porosity (%)	BD (g/cm^3)	PH	Pzc	SA (m^2/g)	
Teff husk	Acid activation	58.42	51.2	10.1	17.5	21.2	42.5	0.549	6.78	5.1	327	This work
Coffee husk	»	57.0	71.1	6.3	9.4	13.2	57.3	0.690	5.4	4.2	–	TESHOME (2015)
Corn cob	»	55.7	24.8	10.5	1.5	78.2	48.8	0.287	6.2	–	–	Tesfaye (2016)
Rice husk	»	–	–	13.8	38.0	–	12	0.68	6.5	–	105.4	Singh and Singh (2012)

CY carbon yield, *FC* fixed carbon, *MC* moisture content, *AC* ash content, *VM* volatile matter, *BD* bulk density, *SA* surface area, P^{ZC} point of zero charge

Table 4 Selected levels of process parameters used in optimization through three level central composite design

Process parameters	Selected levels for optimization		
	Low (− 1)	Medium (0)	High (+ 1)
pH [*A*]	1.00	2.00	3.00
Initial concentration of Cr(VI) [*B*] (in mg/L)	50.00	100.00	150.00
Adsorbent dose [*C*] (in g/L)	15.00	20.00	25.00
Contact time [*D*] (in h)	1.50	2.00	2.50

agro-wastes. Lower ash, volatile matter, and moisture content of THAC indicate as it is highly porous (Kebede and Gashaw 2016), contain lower non-carbonaceous content, and hydrophobic in its nature, respectively (Tesfaye 2016). The high carbon yield and fixed carbon of THAC were also supportive for the feasibility of production of THAC adsorbent (Mussatto et al. 2010). The carbon yield of THAC is also significantly higher than those observed for other lignocellulose materials such as coffee husk and corncob-based activated carbons (Tesfaye 2016; TESHOME 2015). According to American Water Work Association, to the feasibility practical use of an activated carbon, it's the bulk density should not to be less than 0.25 g/cm^3 (Devi et al. 2012). The bulk density and porosity of the prepared THAC were found to be 0.549 g/cm^3 and 42.5% as stated in Table 3, which is enough porous with higher surface area and satisfies the above condition. The p^H and p^{zc} of the prepared activated carbon become 6.78 and 5.1, respectively (Table 3). The cause for acidic p^{zc} of prepared Teff husk activated carbon may be due to the presence of acidic functional groups such as carboxyl, phenolic, and others on the surface of THAC (TESHOME 2015).

The surface functional groups of THAC that show the change after loading of Cr(VI) were determined. As shown in Fig. 1, the strong peaks of IR spectra were observed at 3466 cm^{-1}, 1631 cm^{-1}, and 1106 cm^{-1} and represents the presence of hydroxyl (-OH), unsaturated C=C, –C–O– groups on the surface of THAC, respectively; which plays a great role in the adsorption process. In the present study, FT-IR spectrum shows that the transmittance band observed at 1106 cm^{-1} decreases to 1095 cm^{-1} after adsorption. This shift can be enlightened by the formation weak and broken bands of –C–O, which resulted from Cr(VI) bonding with carbonyl groups, could not be observed in the spectrum. Therefore, it can be considered as Cr(VI) ion may be chemically adsorbed on the surface of the THAC (Sencan and Kiliç 2015). These functional groups were also found in other agro-waste-based activated carbons (TESHOME 2015; Tadesse et al. 2015).

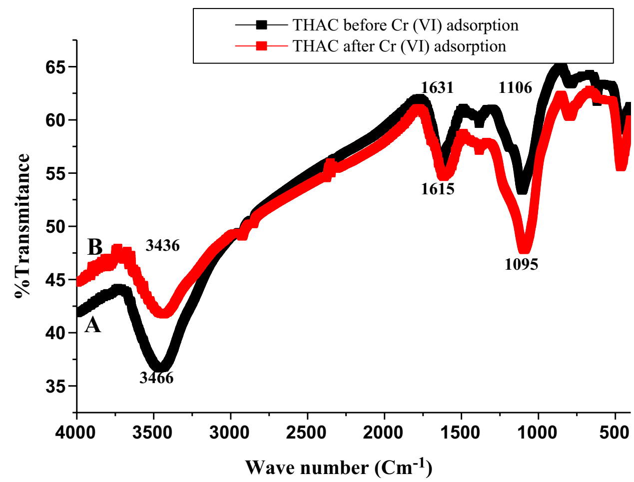

Fig. 1 FT-IR spectra of THAC in KBr disk; **a** before Cr(VI) adsorption and **b** after Cr(VI) adsorption

Effect of experimental parameters on adsorption of Cr(VI) on the THAC

Effect of solution pH on adsorption

The current study depicted that uptake of Cr(VI) decreases with increasing pH as shown in Fig. 2a. This might be due to at lower pH, number of OH^- groups becomes decrease, and the net positive charge of activated carbon becomes increase. This leads to high electrostatic force for the adsorption of chromate anions (acid chromate ($HCrO_4^{\ -}$), chromate (CrO_4^{2-}), and dichromate ($Cr_2O_7^{2-}$) ions) on the positive surface of activated carbon (Mullick et al. 2017; Kakavandi et al. 2014; Dula et al. 2014). Maximum Cr(VI) removal efficiency was obtained at pH 2, which is in line with the actual pH of most industrial effluents such as tannery, electroplating, and chromium plating effluent. This depicts that THAC can be used as the best choice for removal of Cr(VI) from most industrial effluents (Alemayehu et al. 2011). While application of THAC for treatment of effluents with higher pH, adjustment of the pH would be required prior to adsorption (Itankar and Patil 2014). The finding was in close agreement with other studies (Dula et al. 2014; Renuga et al. 2010; Singh and Singh 2012; Zhang et al. 2012; Tadesse et al. 2015).

Effect of initial concentration of Cr(VI) on adsorption

The result shown in Fig. 2b shows that as the initial concentration of Cr(VI) increases, its removal efficiency becomes decrease. At higher concentration, the available sites of adsorption to initial number of metals become fewer and the removal efficiency becomes decreased (Tadesse et al. 2015). The maximum removal efficiency was also achieved

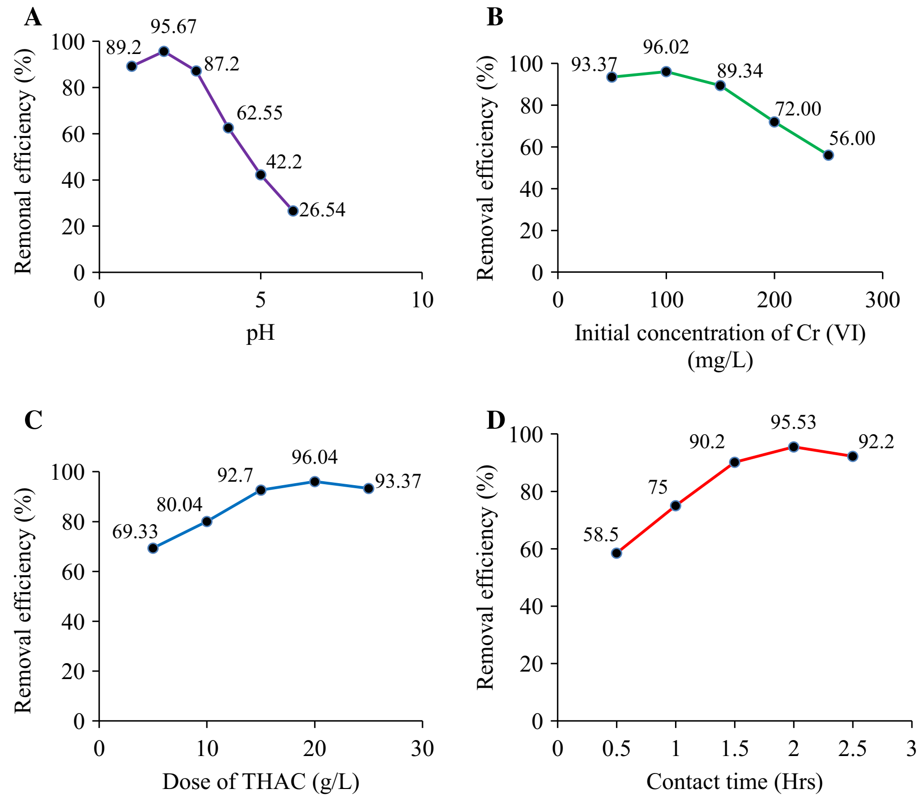

Fig. 2 Effect of **a** pH, **b** initial conc. of Cr(VI), **c** dose of THAC, **d** contact time on the Cr(VI) removal efficiency of THAC: adsorption condition: volume of solution 100 mL, pH 2, Cr(VI) conc. 100 mg/L, amount of THAC 2.0 g, contact time 2 h, and temperature 25 °C

at 100 mg/L initial concentration of the metal. This result is also in agreement with other studies conducted on different agro-waste-based ACs (Dula et al. 2014; Berihun 2017).

Effect of adsorbent dose on adsorption

As clearly shown in Fig. 2c, the removal efficiency of THAC becomes increase with increase in the dose of activated carbon. This may be due to the availability of more adsorption sites for the metal ions (Emirie 2015; Gnanasundaram et al. 2017). But further increase in dose of activated carbon leads to decrease in the removal efficiency. This may also due to instauration of the active sites on the adsorbent surface and aggregation resulting from high adsorbate concentrations (Kakavandi et al. 2014; Tesfaye 2016). The maximum removal efficiency was also achieved with an adsorbent dose of 20 g/L or 2 g/100 ml of solution. This finding is also consistent with other studies (Kebede and Gashaw 2016; Azimi et al. 2017; Devi et al. 2012).

Effect of contact time on adsorption

In this study, the removal efficiency of THAC increases with increasing the contact time. But it starts to fall down for an increase in time beyond the equilibrium time. This is because the extent of adsorption increased rapidly in the initial stages due to the presence of large number of unoccupied active sites of an activated carbon. But after a certain time, most sites may be occupied and the remaining sites may be difficult to occupy because of repulsive forces between adsorbate ions on the solid and in the solution (Devi et al. 2012). The maximum removal efficiency was achieved at the equilibrium point after 2 h contact time. This finding is also in agreement with other studies conducted on agro-waste activated carbons.

Optimum condition for Cr(VI) removal using THAC

Chromium (VI) adsorption modeling and model analysis

The three levels of each four process parameters were selected based on the highest removal efficiency from batch adsorption experiment. The response surface methodology and CCD were used to select the model and to optimize adsorption conditions.

The interaction effect of four studied variables pH (A), initial concentration of Cr(VI) (B), adsorbent dose (C), and contact time (D) on the removal efficiency of Cr(VI) was studied with 30 random experimental runs generated by CCD. The adsorption of Cr(VI) on THAC in terms of removal efficiency was found to be in range from 76.27 to 95.77% (Table 5). The actual removal efficiency was also found in close agreement with the predicted removal efficiency of THAC.

Table 5 Experimental design matrix generated by CCD for removal of Cr(VI) on *Teff* husk activated carbon

Standard order	Run order	Actual variables				Removal efficiency (%)		Relative error
		A	B	C	D	Experimental	Predicted	
11	1	1.00	150.00	15.00	2.50	76.27	76.18	0.09
30	2	2.00	100.00	20.00	2.00	95.77	95.22	0.55
15	3	1.00	150.00	25.00	2.50	78.12	78.15	−0.03
24	4	2.00	100.00	20.00	2.50	91.84	91.71	0.13
27	5	2.00	100.00	20.00	2.00	95.17	95.22	−0.05
22	6	2.00	100.00	25.00	2.00	93.17	93.10	0.07
4	7	3.00	150.00	15.00	1.50	73.23	73.16	0.07
18	8	3.00	100.00	20.00	2.00	87.17	87.05	0.12
5	9	1.00	50.00	25.00	1.50	78.05	78.00	0.05
23	10	2.00	100.00	20.00	1.50	89.84	89.87	−0.03
10	11	3.00	50.00	15.00	2.50	81.01	81.04	−0.03
8	12	3.00	150.00	25.00	1.50	77.67	77.68	−0.01
16	13	3.00	150.00	25.00	2.50	76.34	76.33	0.01
12	14	3.00	150.00	15.00	2.50	73.23	73.30	−0.07
26	15	2.00	100.00	20.00	2.00	95.17	95.22	−0.05
6	16	3.00	50.00	25.00	1.50	77.11	77.19	−0.08
13	17	1.00	50.00	25.00	2.50	81.01	81.07	−0.06
29	18	2.00	100.00	20.00	2.00	95.17	95.22	−0.05
17	19	1.00	100.00	20.00	2.00	89.17	89.20	−0.03
25	20	2.00	100.00	20.00	2.00	94.81	95.22	−0.41
21	21	2.00	100.00	15.00	2.00	91.84	91.81	0.03
19	22	2.00	50.00	20.00	2.00	93.01	92.85	0.16
28	23	2.00	100.00	20.00	2.00	94.91	95.22	−0.31
3	24	1.00	150.00	15.00	1.50	75.45	75.49	−0.04
7	25	1.00	150.00	25.00	1.50	79.00	78.96	0.04
14	26	3.00	50.00	25.00	2.50	79.68	79.67	0.01
2	27	3.00	50.00	15.00	1.50	77.01	77.02	−0.01
1	28	1.00	50.00	15.00	1.50	78.99	78.99	0
20	29	2.00	150.00	20.00	2.00	88.78	88.85	−0.07
9	30	1.00	50.00	15.00	2.50	83.68	83.71	−0.03

A pH; *B* initial concentration of Cr(VI) (mg/L), *C* dose of activated carbon (g/L), *D* contact time (h)

The quadratic model was found to be the highest order polynomial function with maximum adjusted R-squared value (0.9994) (Table 6) and was selected as the best model to represent chromium (VI) efficiency of THAC. This is also consistent with the studies conducted on the removal of Cr(VI) using different agro-waste-based activated carbons (Emirie 2015; Gnanasundaram et al. 2017; Aravind et al. 2016).

ANOVA and Log transformed second-order quadratic regression

Different diagnostic and influence plots were also examined to test the effect of outliers and satisfaction of the assumptions of the analysis of variance. All plots revealed that the model has satisfied the assumption of ANOVA (Annex 2 in supplementary material). As given in Table 7, the ANOVA test was performed to examine the

Table 6 Model summary statistics for removal of Cr(VI) on Teff husk activated carbon

Source	SD	R^2	Adjusted R^2	Predicted R^2	PRESS	RE
Linear	0.0981	0.0555	−0.0957	−0.3524	0.3447	
2FI	0.1111	0.0806	−0.4033	−2.5672	0.9092	
Quadratic	0.0023	0.9997	0.9994	0.9994	0.0002	Selected
Cubic	0.0031	0.9997	0.9989	0.9976	0.0006	Aliased

Table 7 ANOVA table for removal efficiency (natural log transformed removal efficiency)

Source	DF	Sum of squares	Mean square	*F* value	Prob > *F*
Model	14	0.254802	0.0182	3490.03	< 0.0001
A	1	0.00268	0.00268	513.87	< 0.0001
B	1	0.008733	0.008733	1674.58	< 0.0001
C	1	0.000872	0.000872	167.19	< 0.0001
D	1	0.001852	0.001852	355.16	< 0.0001
AB	1	3.69E−05	3.69E−05	7.0850	0.0178
AC	1	0.000222	0.000222	42.58	< 0.0001
AD	1	5.06E−05	5.06E−05	9.69	0.0071
BC	1	0.003311	0.003311	634.96	< 0.0001
BD	1	0.002407	0.002407	461.53	< 0.0001
CD	1	0.000378	0.000378	72.41	< 0.0001
A^2	1	0.015535	0.015535	2978.96	< 0.0001
B^2	1	0.005774	0.005774	1107.28	< 0.0001
C^2	1	0.002242	0.002242	429.99	< 0.0001
D^2	1	0.005879	0.005879	1127.31	< 0.0001
Residual	15	7.82E−05	5.21E−06		
Lack of Fit	10	1.64E−05	1.64E−06	0.133	0.9964
Pure Error	5	6.18E−05	1.24E−05		
Cor Total	29		0.25488		

A pH; *B* initial concentration of Cr(VI), *C* dose of activated carbon, *D* contact time

significance of the individual factors and their interaction on the removal efficiency of THAC. *p* values less than 0.05 indicate model terms were significant. In this study, *A*, *B*, *C*, *D*, *AB*, *AC*, *AD*, *BC*, *BD*, *CD*, A^2, B^2, C^2, D^2 were significant model terms. This indicated that all the parameters are significant process parameters to the removal efficiency of THAC. This finding is also in agreement with other studies conducted on agro-waste-based activated carbons (Tesfaye 2016; Gnanasundaram et al. 2017, Aravind et al. 2016). Log transformed second-order quadratic regression was also done to estimate the removal efficiency as a second-order polynomial function of four independent process parameters. By default, the high levels of the factors were coded as + 1 and the low levels are coded as − 1. The *coded equation* is useful for identifying the relative impact of the factors by comparing the factor coefficients (Aravind et al. 2016).

Estimation of combined effects of the factors

The CCD method is used to examine the significant effects of the process parameters (pH, initial concentration, adsorbent dose, and contact time) on the removal efficiency of Cr(VI). By making other variables constant, the effect of interaction of two variables at a time on the responses was investigated and presented below using contour plots and 3D response surface.

Figure 3a illustrates the 3D plot of combined effect of pH and initial concentration of Cr(VI) at constant adsorbent dosage (20 g/L) and contact time (2 h). The removal efficiency gets increase with decrease in pH until pH 2, and it starts to decline for further lower pH. The removal efficiency also becomes increase with increase adsorbent dose until it reaches 20 g/L and decrease with further addition of adsorbent dose. As stated from coded equation of the response variable, the combined effect of pH and initial concentration of Cr(VI) (*A*, ***B***) affect the removal efficiency negatively with the coefficient of − 0.0015 (Eq. 2). It also has a significant effect on removal efficiency with *p* value of 0.0178 (Table 7). The maximum removal efficiency at all the studied concentrations takes place at pH 2 and at initial concentration of 100 mg/L.

The interaction between pH and adsorbent dose on Cr(VI) removal efficiency of THAC is presented in Fig. 3b. The removal efficiency gets increase with decrease in pH until pH 2, and it starts to decline for further lower pH. It also becomes increase with increasing adsorbent dose until it reaches 20 g/L and decrease with further addition of adsorbent dose. As stated from coded equation of the response variable, the combined effect of pH and adsorbent dose (*A*, *C*) affects the removal efficiency positively with the coefficient of + 0.0037 (Eq. 2). It also has a significant effect on removal efficiency of THAC with *p* value of less than 0.001 (Table 7). The maximum adsorption of Cr(VI) ion is obtained at pH 2 and *AC* dose of 20 g/L.

Figure 3c shows that the effect of solution pH and contact time on the removal efficiency of THAC was significant. The removal efficiency of THAC was increased with increase in contact time until is equilibrium point. It also becomes increase with increasing contact time until it reaches 2 h and decrease with further increase in contact time. As stated from coded equation of the response variable, the combined effect of pH and contact time (*A*, *D*) affects the removal efficiency negatively with the coefficient of − 0.0018 (Eq. 2). It

$$\begin{aligned}\text{Ln (removal efficiency) (\%)} = {} & 4.56 - 0.0122A - 0.0220B + 0.0070C + 0.0101D \\ & - 0.0015AB + 0.0037AC - 0.0018AD + 0.0144BC - 0.0123BD - 0.0049CD \\ & - 0.0774A^2 - 0.0472B^2 - 0.0294C^2 - 0.0476D^2 \quad \text{coded equation}\end{aligned} \tag{2}$$

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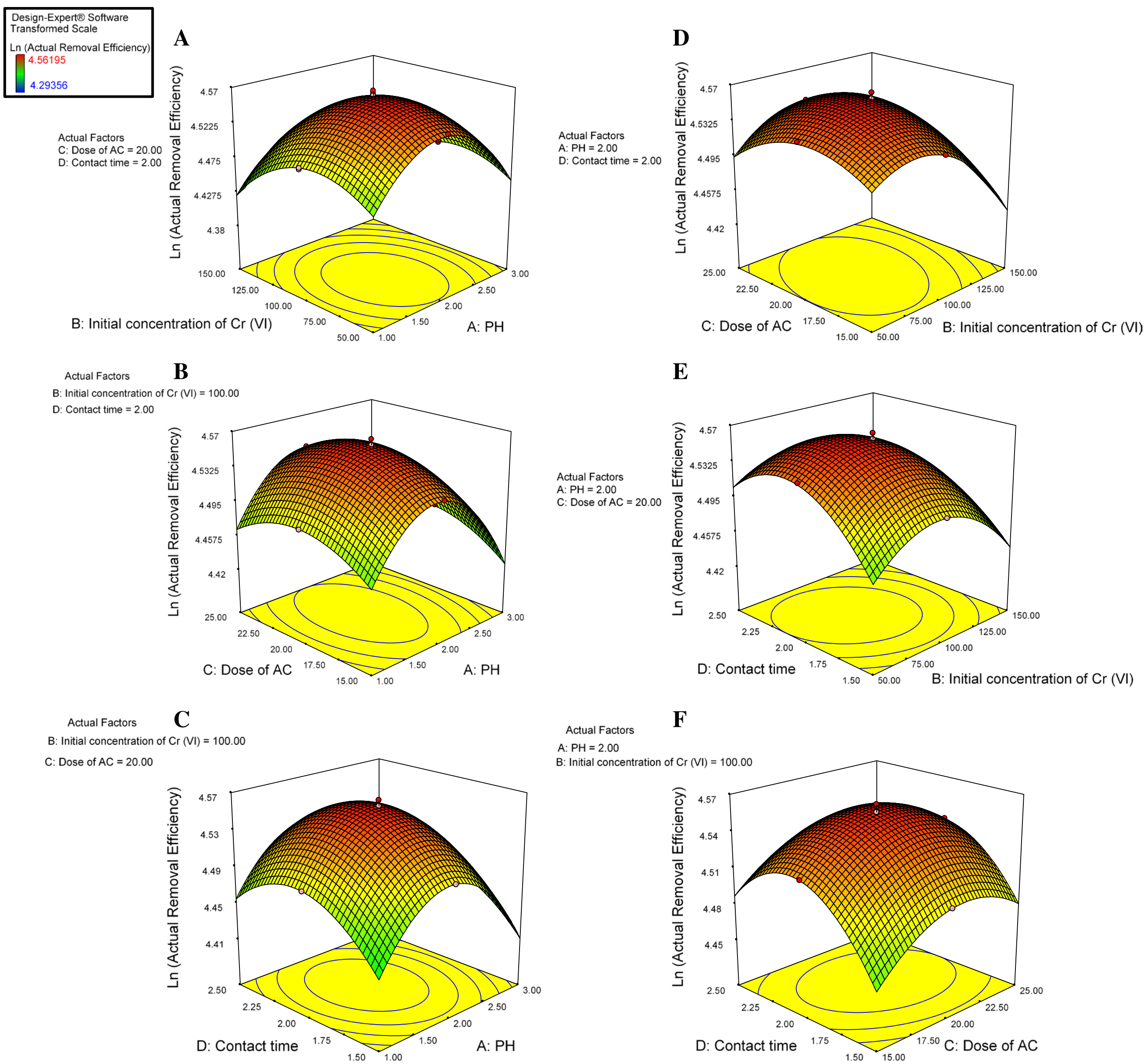

Fig. 3 3D response surface plot of combined effect of **a** PH and initial concentration of Cr(VI). **b** PH and dose of activated carbon: on removal efficiency of THAC. C) PH and contact time. D) Initial concentration of Cr(VI) and dose of activated carbon on removal efficiency of THAC. E) Initial concentration of Cr(VI) and contact time. F) Dose of activated carbon and contact time: on removal efficiency of THAC

also has a significant effect on removal efficiency of THAC with p value of 0.0071 (Table 7). The maximum removal efficiency was achieved at pH 2 and contact time of 2 h.

The combined effect of initial Cr(VI) concentration and adsorbent dose on removal efficiency of THAC is shown in Fig. 3d. From the plots, it can be seen that the removal efficiency increases with decrease in the initial Cr(VI) concentration from 150 to 100 mg/L and increase in adsorbent dose from 15 to 20 g/L. As stated from coded equation of the response variable, the combined effect of initial Cr(VI) concentration and adsorbent dose (B, C) affect the removal efficiency positively with the coefficient of $+0.0144$ (Eq. 2). It also has a significant effect on removal efficiency of THAC with p value of less than 0.001 (Table 7). The maximum removal efficiency was achieved at initial Cr(VI) concentration from 100 mg/L and adsorbent dose of 20 g/L.

The interaction effect of initial Cr(VI) concentration and contact time on the removal efficiency of THAC is shown in Fig. 3e. The figure revealed that as the contact time increases from 1.5 to 2.0 h, the removal efficiency becomes increased and becomes decreased for longer contact time. As stated from coded equation of the response variable, the combined effect of initial Cr(VI) concentration and contact time (B&D) affects the removal efficiency negatively with the coefficient of −0.0123 (Eq. 2). This result is also supported by the ANOVA result which showed that the interaction of initial metal Cr(VI) concentration and contact time has significant effect on the removal efficiency with the *p* value of less than 0.001 (Table 7). Therefore, the interaction between contact time and initial metal Cr(VI) concentration has a significant effect on the removal efficiency of THAC.

The combined effect of adsorbent dose and contact time on the removal efficiency of THAC is shown in Fig. 3g. From the plots, it can be seen that the removal efficiency increases with adsorbent dose from 15 to 20 g/L and increasing contact time from 1.5 to 2.0 h. As stated from coded equation of the response variable, the combined effect of adsorbent dose and contact time (*C*, *D*) affects the removal efficiency negatively with the coefficient of −0.0049 (Eq. 2). It also has a significant effect on removal efficiency of THAC with *p* value of less than 0.001 (Table 7). It also revealed that the maximum removal efficiency was achieved at an adsorbent dose of 20 g/L and 2.0 h contact time.

Optimized condition for Cr(VI) removal and validation experiments

An experiment was conducted to evaluate the optimization result under optimum conditions predicted by the model. The actual experimental removal efficiency of THAC at the optimum condition was in close agreement with model predicted value (Table 8). Therefore, the optimization conditions were validated.

Adsorption mechanism

Adsorption isotherm models

The Langmuir and Freundlich isotherms were used to describe the mechanism in which the metal ions and active surfaces of an adsorbent are interacted together (Ong et al. 2010).

Langmuir Isotherm according to Langmuir adsorption theory, active sites of adsorbent are homogeneously distributed and the adsorption is monolayer. This is better isotherm to explain chemical adsorption (Abas et al. 2013). The isotherm is represented by:

$$\frac{C_e}{q_e} = \frac{1}{bq_{max}} + \frac{C_e}{q_{max}} \tag{3}$$

The fitness of this isothermal model can be determined from the linear plot of specific adsorption (C_e/q_e) against the equilibrium concentration (C_e) as plotted in Fig. 4a. The values of constants, the energy of adsorption (*b*), and maximum adsorption capacity (q_{max}) can be determined from the slope and intercept of the plot (Desta 2013).

Freundlich isotherm model assumes as the active sites of surfaces are heterogeneous; there is an interaction between adsorbed molecules and not restricted to the formation of a monolayer (Abas et al. 2013). The fitness of the model was tested using the linearized equation of Freundlich model:

$$\ln q_e = \ln K_f - \frac{1}{n} \ln C_e \tag{4}$$

where q_e represents the amount adsorbed per amount of adsorbent at the equilibrium (mg/g), C_e represents the equilibrium concentration (mg/L), and adsorption capacity (K_f)

Table 8 Optimum conditions of the four studied parameters for removal of Cr(VI) by THAC

Process parameters	pH	Initial conc. of Cr(VI)	Dose of AC	Contact time	Removal efficiency		Desirability
					predicted (%)	actual (%)	
Optimized condition	1.92	87.83 mg/L	20.22 g/L	2.07 h	95.60%	95.57%,	0.993

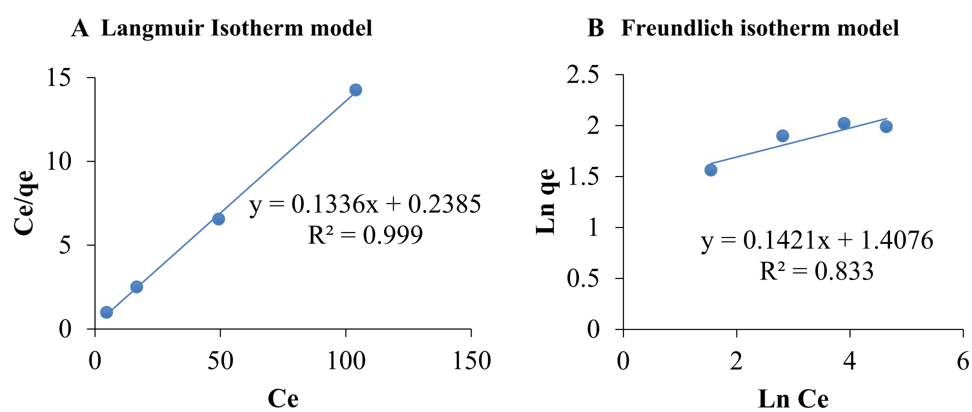

Fig. 4 Plot of **a** Langmuir isotherm model, **b** Freundlich isotherm model fitness at conditions of: volume of solution = 100 mL, initial Cr(VI) concentration = 100, 150, 200, 250 mg/L, pH = 2, amount of THAC = 2 g, contact time = 2h at temperature of 25 °C

and adsorption intensity (n) are Freundlich constants whose value can be determined from the plot of ln q_e versus ln C_e as plotted in Fig. 4b.

Results stated on Fig. 4 revealed that the higher correlation coefficient is observed using the Langmuir isothermal model. This implies that the model is best fitted to explain Cr(VI) adsorption on THAC. So the active sites of THAC were homogeneously distributed and the adsorption was monolayer and chemical adsorption (Emirie 2015).

Adsorption kinetics models

Adsorption kinetics represents the solute removal rate. Information on adsorption kinetics can also be used to select the optimum condition for full-scale removal processes design (Tesfaye 2016).

Pseudo-first order kinetics model refers to the assumption of the rate of change of solute uptake with time which is directly proportional to the difference in the saturation concentration and the amount of solid uptake with time. The fitness of pseudo-first order kinetic model was tested using the linearized equation of Lagergren model is given by (Emirie 2015):

$$\log\left(q_e - q_t\right) = \log q_e - \frac{K_1}{2.303}t \quad (5)$$

where q_e and q_t are the amount of adsorbed adsorbate (mg/g) at an equilibrium and at any instant of time t (min), respectively, and k_1 is the rate constant of pseudo-first order adsorption operation (min^{-1}). The values of K_1 and q_e can be determined from the slop and intercept of the plot of log ($q_e - q_t$) versus t, respectively, as plotted in Fig. 5a.

Pseudo-second-order Kinetics model is based on the assumption that the rate limiting step may stem from the chemical adsorption involving valence forces through the sharing or exchange of electrons between the adsorbent and adsorbate. The fitness of pseudo-second-order kinetic model was tested with the linearized equation given as (Emirie 2015):

$$\frac{t}{q_t} = \frac{1}{K_2\left(q_e\right)} + \frac{1}{q_e}t \quad (6)$$

where K_2 is the rate constant of pseudo-second-order adsorption operation. The values of K_2 and q_e can be determined from the slop and intercept of the plot of t/q_t versus t, respectively, as plotted in Fig. 5b.

Results on Fig. 5a, b show that higher correlation was observed by using the pseudo-second-order equation. This implies the pseudo-second-order model provides the best correlation of the data. So the rate limiting step may be caused by chemisorption involving valency forces through sharing or exchange of electrons between adsorbent and adsorbate. The result of isotherm and kinetics studies was also in agreement with other studies conducted to examine the kinetics of Cr(VI) on activated carbon (Mullick et al. 2017; TESHOME 2015; Tadesse et al. 2015).

Final fate of Cr(VI) adsorbed THAC

Since chromium is non-renewable and finite natural resource, application of THAC is not limited for its removal from the wastewater but also outspreads to recovery and recycling of chromium for chrome tanning and other industrial purposes (Itankar and Patil 2014). Therefore, chromium will be recovered and back returned to industry.

Limitation of the study

In this study, the adsorption was conducted in batch adsorption manner due to short period of the study, so the adsorption is not conducted in column adsorption process which is better fit to design in industries.

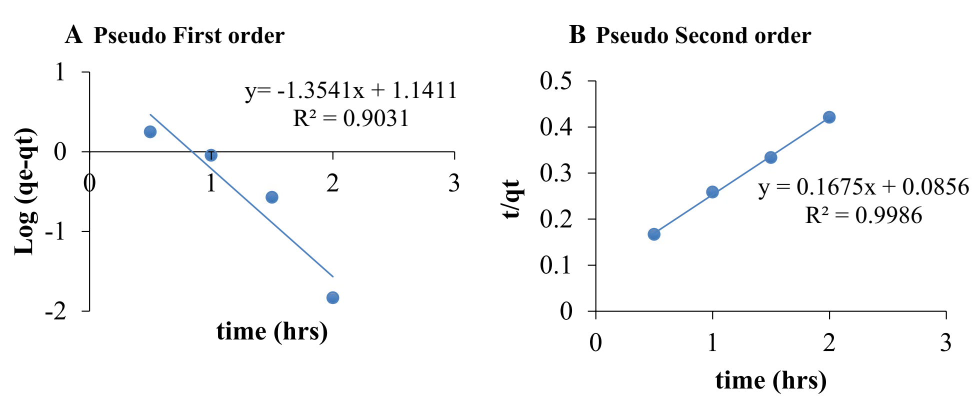

Fig. 5 Plot of **a** pseudo-first order kinetic and **b** pseudo-second-order kinetic models at conditions of: volume of solution = 100 mL, initial Cr(VI) concentration = 100 mg/L, pH = 2, amount of THAC = 2 g, contact time = 0.5, 1.0, 1.5, 2.0 h at temperature of 25 °C

Conclusion and recommendation

The present study focused on the application of Teff husk activated carbon as an effective and locally available adsorbent for removal of hexavalent chromium from aqueous solution. The optimum Cr(VI) removal efficiency of THAC (95.597%) was achieved at pH 1.92, initial concentration of 87.83 mg/L, adsorbent dose of 20.22 g/L, and contact time of 2.07 h. The adsorption of Cr(VI) on to THAC was best fitted to pseudo-second-order kinetics model ($R^2 = 0.9986$) and Langmuir isotherm model ($R^2 = 0.999$). In conclusion, THAC can be used as an effective, locally available, economical, and environmental friendly adsorbent for removal Cr(VI) removal from contaminated water. Column adsorption needs to be studied in future.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

Consent for publication All authors read and approved the manuscript.

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