Taguchi Parametric Optimization and Cost Analysis of Hexavalent Chromium Sequestration From Aqueous Solution by NaOH-Modified *Garcinia kola* Hull Particles

Lekan Taofeek Popoola ⓘD

Separation Processes Research Laboratory, Department of Chemical and Petroleum Engineering, Afe Babalola University, Ado-Ekiti, Ekiti State, Nigeria.

ABSTRACT: The presence of chromium in industrial wastewater is unavoidable due to its large usage as part of chemical constituents used in many industries. Its removal from wastewater is imperative because it's toxic in nature. This study investigated the application of NaOH-modified *Garcinia kola* hull particles (cMGK-HP) for Cr(VI) sequestration from aqueous solution. The optimization of process parameters was executed using Taguchi of Design Expert software for optimum point prediction, analysis of variance, parameters interaction and mathematical model development. A proposed model was used for the adsorption cost analysis. The predicted and experimental percentage of Cr(VI) sequestration were recorded at optimum point to be 99.02% and 98.76% with pH, adsorbent dose, contact time, initial concentration, and temperature of 2, 8 g/L, 20 minutes, 10 mg/L, and 20°C respectively. A correlation coefficient of .9937 between experimental and predicted values of percentage Cr(VI) sequestration affirmed high efficacy of the developed model. ANOVA showed the order of parameter contribution to be pH > adsorbent dose > initial concentration > contact time > temperature. A maximum adsorption capacity of 217.39 mg g^{-1} was obtained for cMGK-HP. Cost analysis revealed using cMGK-HP to be cost effective for Cr(VI) sequestration with a total operational cost of 0.824 \$/mole Cr(VI) ions when compared with commercial activated carbon. Adsorbent characterization revealed the presence of active functional groups enhancing the sequestration process. It could be deduced that cMGK-HP is effective to remove Cr(VI) from solution.

KEYWORDS: Garcinia kola, optimization, sequestration, cost analysis, adsorption

Introduction

The recent progress in global industrialization has greatly influenced the volume of wastewater generated from industries which is constituting nuisance when discharged into nearby environment. Chromium is among the essential constituents of materials used in wood preserving, electroplating, steel fabricating, paints, metal finishing, tanneries and canning industries.[1] This makes chromium to be unavoidably present in the wastewater discharged from these industries into the environment which then finds its way into rivers and ground water via surface runoff and permeation.[2] Due to its mutagenic and carcinogenic nature, it can adversely affect human respiratory tract, liver, kidney and gastrointestinal systems at low concentration above the permissible WHO standard.[3] Therefore, treatment of wastewater from these industries to remove chromium and other hazardous constituents is very important.

Adsorption was chosen as an effective method for pollutants removal from solution because of its operational simplicity, low cost, high sequestration efficiency and low energy consumption. Studies are now looking into synthesizing effective low cost adsorbents from agricultural bye-products such as chickpea,[4] sugar cane bagasse,[5] rice husk,[6] rice bran,[7] rice straw,[8] biochar,[9] *Areca catechu*,[10] and so on as against the costly commercial activated carbon being used in the treatment of industrial wastewater. Their potential lies in the active functional groups such as hydroxyl, carbonyl, carboxylic, amino, and alkoxy that are present in them. Nonetheless, their surface also possess active mesopores

that create allowance for the adsorption of heavy metals from solution. The study conducted by Rambabu et al[11] revealed mesopores of *Phoenix dactylifera* coir biosorbent to be highly rich in cellulose containing varieties of active functional groups that would enhance its surface for hexavalent chromium ions sequestration after volarization. A similar study by Bharath et al[12] used a simple pyrolysis method to synthesize mesoporous date seed-derived activated carbon used as an anode in a cell that was assembled with Ti_3AlC_2 as a cathode to deionize hexavalent chromium ions from industrial effluents. To support the adsorption efficiency of these materials, their chemical modification using NaOH, KOH, HNO_3, H_2SO_4, HCl, and so on helps in improving the number of internal pores available for the adsorption of contaminant.[13,14]

The optimization of process parameters for the adsorption of contaminants in wastewater is essential for proper adsorption column design and effective operational cost minimization.[15] In this study, the optimization of adsorption process parameters and cost analysis of Cr(VI) removal from solution was conducted using NaOH-modified *Garcinia kola* hull particles (cMGK-HP) as adsorbent against previously used adsorbents generated from agrowastes. The hull of *Garcinia kola* is highly rich in protein, fiber and cellulose[16,17]; and also contains bioactive compounds such as flavonoids, alkaloids, tannins, saponins cyanogeinic and glycosides.[18] These are active ingredients essentially needed for removal of heavy metals such as Cr(VI) from solution. Taguchi of the Design Expert was

Table 1. Experimental parameters and their values at different levels.

PARAMETER	UNITS	CODE	LEVEL 1	LEVEL 2	LEVEL 3	LEVEL 4
pH		A	2	4	8	12
Contact time	min	B	20	40	80	120
Adsorbent dose	g/L	C	2	4	8	12
Initial concentration	mg/L	D	10	20	40	60
Temperature	°C	E	20	30	40	60

adopted for the design of experiment (DoE) and also served as the optimization tool for the process. Design of experiment is a multivariate statistical technique which helps in reducing the cost, time and materials needed to conduct laboratory experiments.[19] Taguchi as a DoE and statistical optimization tool is effective in reducing the number of experimental runs, observing the influence of discrete factors on responses and simultaneously determining optimum points for different responses.[20]

The effectiveness of developed mathematical model for prediction of percentage Cr(VI) removal from solution was justified by ANOVA. The influence of single factor and parameter interaction on the hexavalent chromium ion sequestration were studied. The isotherm, kinetics and thermodynamic studies were executed to determine the adsorption nature. The cost analysis of the process from the point of adsorbent preparation to the Cr(VI) removal was investigated. Characterization of the adsorbent before and after the hexavalent chromium removal was executed using Brunauer-Emmett-Teller method, scanning electron microscope and Fourier transform infrared spectrophotometer.

Materials and Methods

Chemicals and stock solution preparation

Analytical grade chemicals were purchased and used without further alteration. A stock solution of 1000 mg/L of Cr(VI) was prepared via dissolving 2.8255 g of $K_2Cr_2O_7$ salt in 1000 mL of distilled water from which 10, 20, 40, and 60 mg/L of Cr(VI) were prepared by diluting with distilled water. 0.1 M of either NaOH or HCl was used to adjust the solution pH.

Adsorbent preparation

Unwanted impurities were removed from collected hulls of *Garcinia kola* via thorough washing with tap water and rinsing with distilled water. The retained water was removed by sun drying for 7 days and subsequent oven-drying for 48 hours at 105°C. Particle size of less than 150 μm was obtained from the mechanically milled *Garcinia kola* hulls via an electric sieve shaker. Alkaline hydrolysis of the sieved particles (200 g) was conducted using 500 mL of 10% NaOH in a round bottom flask at 120 rpm for 3 hours. The particles were thoroughly washed with distilled water till neutrality, filtered and then dried in an oven at 105°C for 24 hours. The filtrate was treated with phenolphthalein to examine the neutrality level. The

NaOH-modified *Garcinia kola* hull particles (cMGK-HP), used as adsorbent, was then stored in a desiccator.

Batch adsorption step

The batch adsorption process was conducted at different parameters' levels (stated in Table 1) on a shaker (Stuart heat-stirrer SB162, China) operated at 160 rpm. Specified adsorbent dose was mixed with 100 mL of Cr(VI) salt solution in a 250-mL flask for the batch experiments. The filtrate and the residue were separated using Whatman filter paper and Cr(VI) concentration was measured via Atomic Adsorption Spectrophotometer (Buck scientific model 210 VGP, USA) operated at a maximum wavelength of 540 nm. A standard solution of 1,5-diphenylcarbazide in acetone was prepared. The percentage of Cr(VI) removed from aqueous solution (*X*, %) and adsorbent sorption capacity (q_e, mg/g) were determined using equations (1) and (2) respectively.

$$X\ (\%) = \frac{(C_o - C_e)}{C_o} \times 100 \tag{1}$$

$$q_e = (C_o - C_e) \times \frac{V}{W} \tag{2}$$

where C_o and C_e = initial and final concentrations of Cr(VI) (mg/L) respectively, V = solution volume (mL) and W = adsorbent weight (g).

Taguchi design of experiment

For model development and measurement of contributory parameters influence on Cr(VI) sequestration from aqueous solution by cMGK-HP, factorial Taguchi orthogonal array of Design Expert 12 was used. Table 1 presents the experimental parameters used and their values at different levels.[21] In all, 16 experimental runs were conducted for 5 parameters having values at 4 different levels.

Regeneration and reusability of cMGK-HP

Regeneration of used cMGK-HP was conducted by washing the adsorbent thoroughly with distilled water until neutrality is attained. The washed cMGK-HP was then dried at 80°C for 6 hours. The reusability efficiency of cMGK-HP for Cr(VI) sequestration from aqueous solution was investigated via

Table 2. Design of experiment by Taguchi indicating parameters' variables and response.

RUN	PH	CONTACT TIME	ADSORBENT DOSE	INITIAL CONCENTRATION	TEMPERATURE	CR(VI) ION SEQUESTRATION (%)	
		MIN	G/L	MG/L	°C	EXPERIMENTAL	PREDICTED
1	4	40	2	60	40	71.01	71.82
2	12	20	12	20	40	72.31	73.18
3	2	40	4	20	30	79.7	80.51
4	12	40	8	10	60	86.37	87.18
5	2	20	2	10	20	84.95	85.82
6	8	120	4	60	40	67.44	66.88
7	2	80	8	40	40	91.08	89.96
8	12	120	2	40	30	61.89	61.33
9	8	40	12	40	20	74.06	74.87
10	8	80	2	20	60	65.64	64.52
11	4	120	12	20	20	90	89.44
12	2	120	8	10	60	97.27	96.71
13	8	20	8	60	30	68.82	69.69
14	4	20	4	40	60	84.81	85.68
15	12	80	4	60	20	68.49	67.37
16	4	80	12	10	30	93.66	92.54

conducting adsorption-desorption experiments consecutively. For the first adsorption experiment, 0.5 g of Cr(VI) ions loaded cMGK-HP was added to 50 mL of 0.1 M HNO_3 solution in a flask for 2 hours at 80°C in order to increase the oxygen-containing functional groups of the regenerated adsorbent.[22] The regenerated cMGK-HP was re-used consecutively for 5 times and the method prescribed by Giri et al[23] was used to calculate the desorption efficiency.

Characterization

The adsorbent was characterized before and after the hexavalent chromium removal using Brunauer-Emmett-Teller method (Nova 11.03A, USA version), scanning electron microscope (SEM/EDX-JEOL-JSM 7600F) and Fourier transform infrared spectrophotometer (Nicolet iS10).

Results and Discussions
Taguchi design of experiment, mathematical model, and statistical analysis

The response at different values of parameters as obtained from Taguchi experimental design is presented in Table 2. All the experimental runs revealed Cr(VI) ion sequestration from solution by cMGK-HP justifying the effectiveness of the adsorbent for the process. At pH, contact time, adsorbent dose, Cr(VI) initial concentration and temperature of 2, 120 minutes, 8 g/L, 10 mg/L and 60°C respectively, 97.27% of Cr(VI) sequestration from solution by cMGK-HP was observed. This favorable removal efficiency could be attributed to low initial concentration
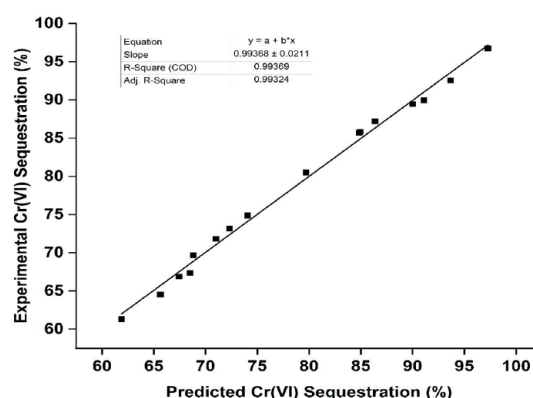

Figure 1. Correlation plot of experimental and predicted values.

of Cr(VI) and maximum mixing time, temperature and adsorbent dosage. For prediction purpose, equation (3) was generated using the Taguchi orthogonal array and was used to determine the predicted values of Cr(VI) ion sequestration presented in Table 2. A correlation coefficient value of .9937 (close to unity), as shown in Figure 1, between the experimental and predicted values justifies the effectiveness of the model for prediction.

$$\begin{aligned}
\text{Cr(VI) ion sequestration (\%)} = & +78.59 + 6.30A[1] \\
& +6.28A[2] - 6.25A[3] - 2.11B[1] \\
& -7.06B[2] + 5.05B[3] - 7.72C[1] \\
& -0.13C[2] + 5.47C[3] + 7.87D[1] \\
& -1.68D[2] - 0.6338D[3] + 0.7813E[1] \\
& -2.58E[2] + 0.22E[3]
\end{aligned} \quad (3)$$

Table 3. Analysis of Variance (ANOVA) for Cr(VI) sequestration by cMGK-HP.

SOURCE	SUM OF SQUARES	*DF*	MEAN	*F*-VALUE	*P*-VALUE	% CONTRIBUTION
Model	1876.99	12	156.42	39.30	.0058	Significant
A-pH	468.72	3	154.11	39.81	.0065	46.83
B-Contact time	41.04	3	13.74	3.49	.1345	4.10
C-Adsorbent dose	352.33	3	121.72	31.38	.0091	35.19
D-Initial concentration	102.81	3	36.51	9.51	.0483	10.27
E-Temperature	36.04	3	11.12	3.12	.1874	3.60
Residual	11.94	3	3.9805			
Cor total	1894.32	15				
			$R^2 = .9937$			
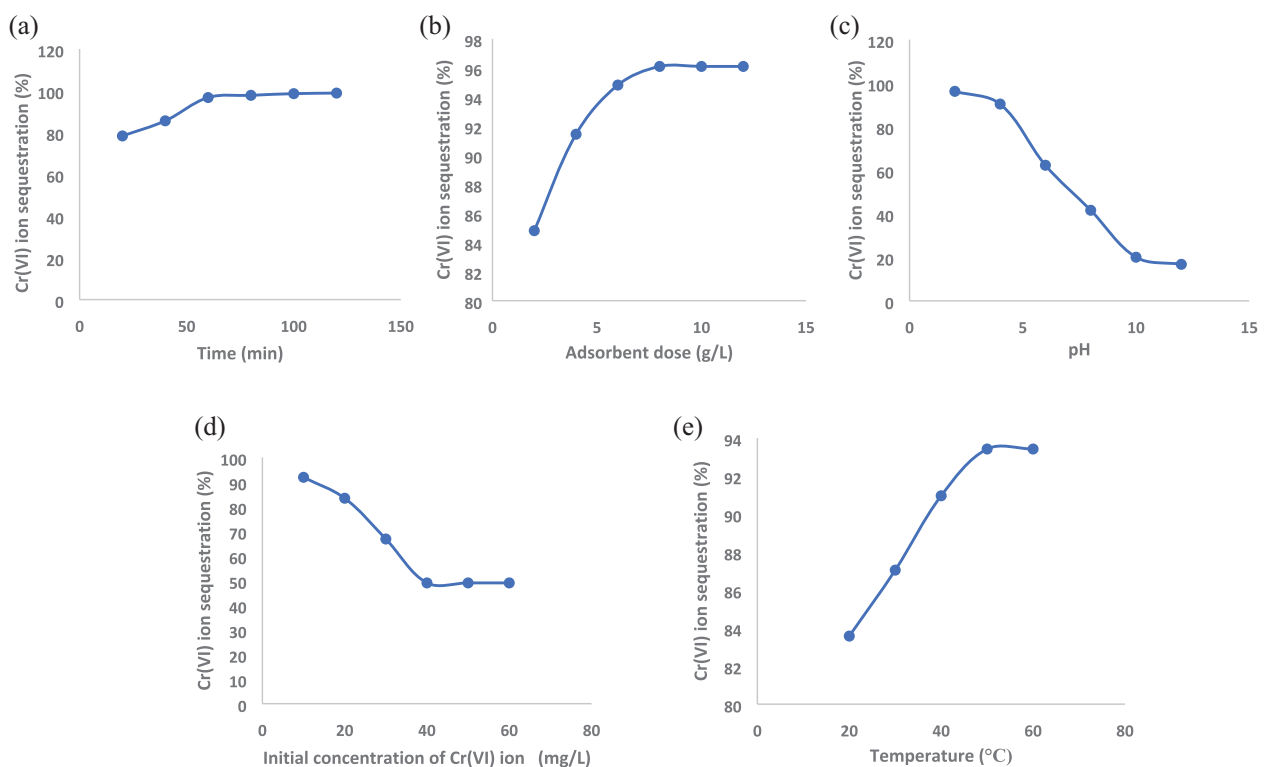
Figure 2. Influence of (a) time, (b) adsorbent dose, (c) pH, (d) Cr(VI) ion initial concentration, and (e) temperature on hexavalent chromium ion sequestration.

Statistical analysis by ANOVA

Table 3 presents the analysis of variance (ANOVA) result for the sequestration process. ANOVA revealed the developed model was significant. The examined parameters were significant to the study with pH exhibiting the highest significant term with *P*-value and F-value of .0065 and 39.81 respectively. A model term is significant when its *P*-value is less than .05. Model term becomes highly significant at lower *P*-value. The percentage contribution of each parameter is calculated using equation (4). The order of experimental parameter contribution to the Cr(VI) ion sequestration from solution by cMGK-HP was pH >adsorbent dose > initial concentration > contact time > temperature with respective percentage of 46.83, 35.19, 10.27, 4.10, and 3.60.

$$Percentage\ contribution = \left[\frac{SS_i}{\sum SS_i}\right] \times 100\% \left(i \neq 0\right) \quad (4)$$

such that SS_i = Sum of square of significant parameter.

Single factor influence on hexavalent chromium ion sequestration

The influence of time, adsorbent dose, pH, Cr(VI) ion initial concentration and temperature on hexavalent chromium ion sequestration are presented as Figure 2. The percentage of Cr(VI) ion removed increased from 78.38% to 98.91% (Figure 2a) when the contact time was increased from 20 to

120 minutes with the attainment of equilibrium after 60 minutes. The bulk of adsorption noticed before this time resulted from higher forces of attraction between the active sites on adsorbent surface and the Cr(VI) ions.[10] As the adsorbent dose was increased from 2 to 12 g/L, the percentage of Cr(VI) ion removed increased from 84.81% to 96.25% (Figure 2b). Equilibrium was attained at adsorbent dose of 8 g/L due to the saturation of the available active sites on adsorbent surface. Increasing solution pH from 2.0 to 12.0 decreased the percentage of hexavalent chromium ion removed from 96.25% to 16.77% (Figure 2c). This observation resulted from active sites dissociation on adsorbent surface due to increase in the concentration of $Cr_2O_7^{2-}$ as the pH deviates from acidic to basic.[21] Increase in the initial concentration of hexavalent chromium ion from 10 to 60 mg/L causes a reduction in the percentage of hexavalent chromium ion removed from 91.91% to 49.03% (Figure 2d) by cMGK-HP due to reduction in the number of active sites on adsorbent surface. Increasing the temperature from 20°C to 60°C increases the percentage of Cr(VI) ion sequestration from 83.58% to 93.42% (Figure 2e) which could be linked to increase in the convective movement of adsorbent particles due to temperature increase.[24]

3D surface plot

Figure 3 depicts the combinatory 3D-surface plots of pH and contact time (Figure 3a), pH and adsorbent dose (Figure 3b), pH and initial concentration (Figure 3c), pH and temperature (Figure 3d), contact time and adsorbent dose (Figure 3e), contact time and initial concentration (Figure 3f), contact time and temperature (Figure 3g), adsorbent dose and initial concentration (Figure 3h), adsorbent dose and temperature (Figure 3i), and initial concentration and temperature (Figure 3j) on the percentage of Cr(VI) removed from solution using cMGK-HP. The percentage of Cr(VI) removed in solution remained constant as the temperature increases with pH (Figure 3a). The percentage of Cr(VI) removed increased as the adsorbent dose was increased but decreased with increase in solution pH (Figure 3b). Decrease in Cr(VI) removal was noticed as the initial concentration and pH were increased (Figure 3c). The percentage of Cr(VI) removed decreased with increase in pH (Figure 3d). As shown in Figure 3e, the percentage of Cr(VI) removed was constant with increase in contact time but increase with increase in adsorbent dose. A decrease in the percentage of Cr(VI) removed was noticed with increase in initial concentration but remain constant with increase in contact time (Figure 3f). The percentage of Cr(VI) removed remained relatively constant with increase in temperature and contact time (Figure 3g). Figure 3h revealed decrease in Cr(VI) removed from solution as the initial concentration was increased and vice versa for adsorbent dose. The Cr(VI) removed from solution remained relatively constant with increase in temperature but increased with increase in adsorbent dose (Figure 3i). The percentage of Cr(VI) was relatively constant with increase in temperature but decreased with increase in initial concentration.
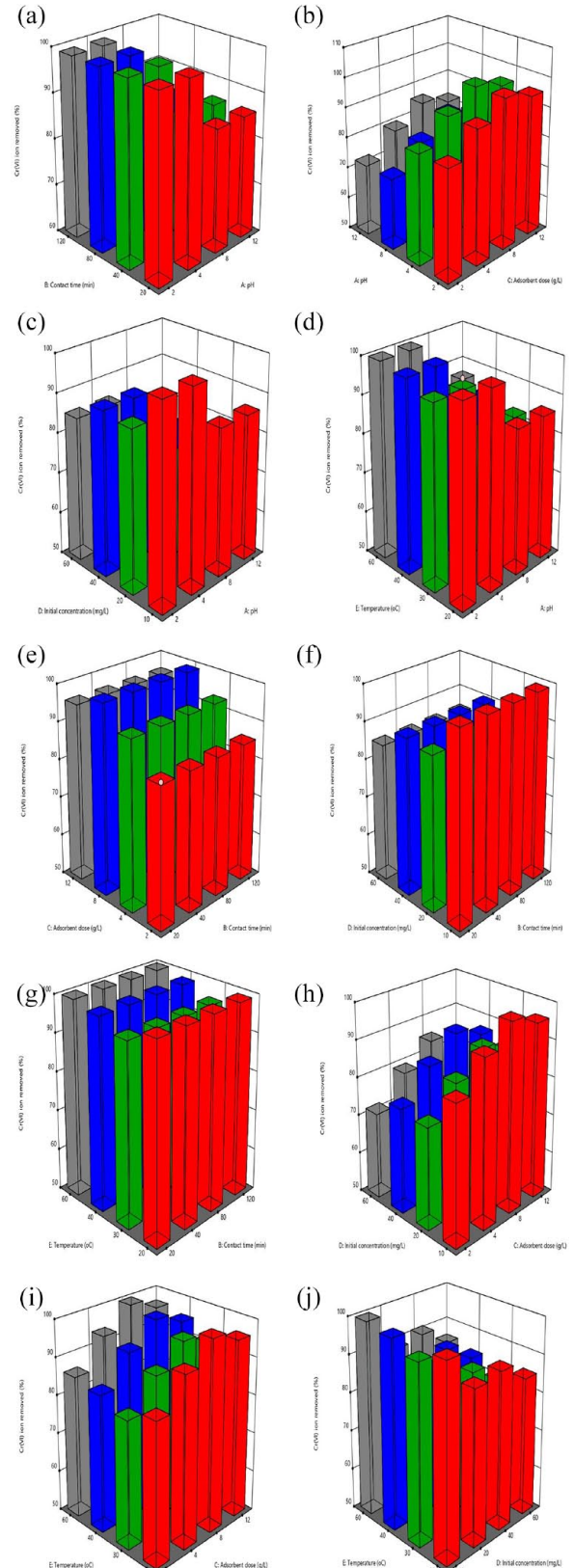

Figure 3. 3D-Surface plot showing the combinatory effect of (a) pH and contact time, (b) pH and adsorbent dose, (c) pH and initial concentration, (d) pH and temperature, (e) contact time and adsorbent dose, (f) contact time and initial concentration, (g) contact time and temperature, (h) adsorbent dose and initial concentration, (i) adsorbent dose and temperature, and (j) initial concentration and temperature on the percentage of Cr(VI) removed from solution.
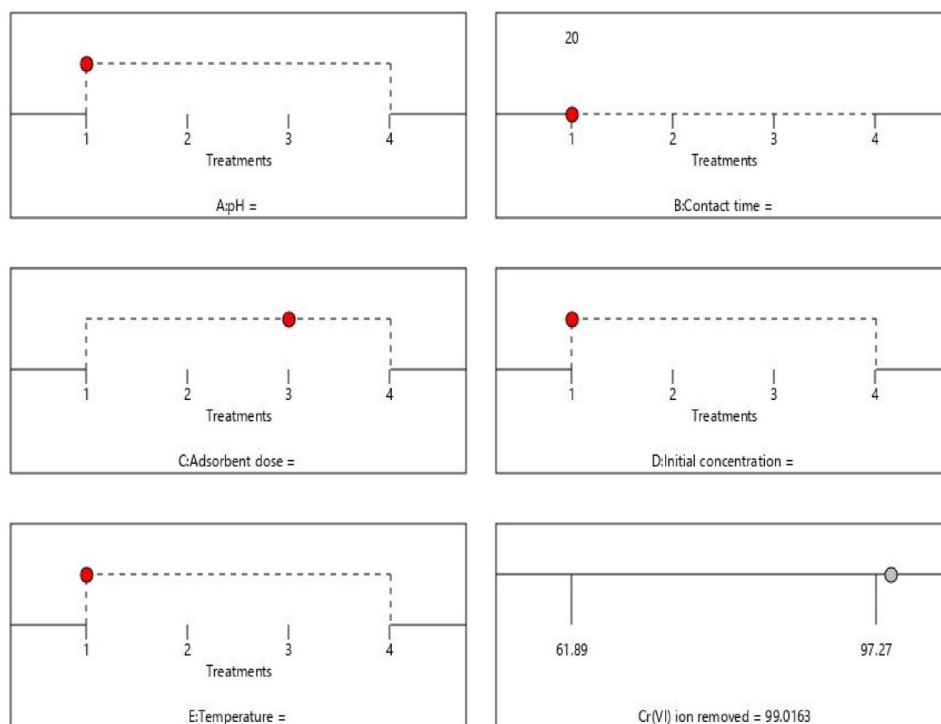
Figure 4. Optimum predicted points by Taguchi at different parameter levels.

Generally, increase in the percentage of Cr(VI) removed with increase in adsorbent dosage resulted from increase in the number of active pores available for the heavy metal removal. The observed decrease in the Cr(VI) removed as the pH was increased could be linked to protonation reduction on the adsorbent surface by H^+ ions causing precipitation of OH^- ions which in return blocked the active sites.[25] A decrease in the percentage of the hexavalent chromium ions removed as its initial concentration was increased resulted from the blockage of the constant number of the active pores available for the adsorption process.[26]

Optimum Point for Cr(VI) sequestration

Figure 4 displays the Taguchi optimum predicted points for Cr(VI) sequestration using cMGK-HK where pH, contact time, adsorbent dose, Cr(VI) initial concentration and temperature were obtained at level 1 (2), level 1 (20 minutes), level 3 (8 g/L), level 1 (10 mg/L), and level 1 (20°C) respectively. The predicted Cr(VI) sequestration from solution by the adsorbent was 99.02%. At this point, laboratory experiment was conducted and 98.76% of Cr(VI) sequestration was observed. Ali and Saeed[27] revealed optimum removal efficiency of 90% at initial concentration, adsorbent dose, pH, and contact time of 3 mg/L, 4 g/L, 6, and 60 minutes respectively using alkaline-hydrolysed banana peels. Rambabu et al[11] reported maximum sequestration efficiency of 87.2% for hexavalent chromium ions applying *Phoenix dactylifera* coir biosorbent at initial concentration, adsorbent dose, pH, contact time, temperature, and agitation speed of 100 ppm, 0.3 g, 2, 60 minutes, 30°C, and 100 rpm respectively. Yusuff et al[9] obtained optimum point at initial concentration, adsorbent dose, pH, and contact time of 10 mg/L, 0.3 g/L, 6, and 140 minutes respectively with 83.2% Cr(VI) sequestration using $ZnCl_2$-modified eucalyptus bark biochar.

Isotherm, kinetics and thermodynamics studies

Equations (5) and (6) represent the linearized forms of Freundlich[28] and Langmuir[29] respectively used for the isotherm study.

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (5)$$

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}} \quad (6)$$

where q_e = adsorption capacity (mg/g), K_F = *Freundlich* isotherm constant ($mg^{1-1/n}$ $L^{1/n}$ g^{-1}), n = heterogeneity constant, C_e = adsorbate equilibrium concentration (mg/L), K_L = Langmuir constant (Lmg^{-1}) and q_{max} = Langmuir maximum adsorption capacity (mg g^{-1}).

Figures 5 and 6 represent the plots of *log* q_e versus *log* C_e (Freundlich) and C_e/q_e versus C_e (Langmuir) respectively. The results obtained revealed R^2 values of .9984 and .8780 for Langmuir and Freundlich respectively suggesting excellent fitness of Langmuir for the experimental data. A maximum adsorption capacity of 217.39 mg g^{-1} was obtained for cMGK-HP. The result was similar to those presented by Ali et al[30] and Parlayici and Pehlivan[31].

Equations (7) and (8) are the linearized pseudo first-order and pseudo second-order kinetic models used in this study.
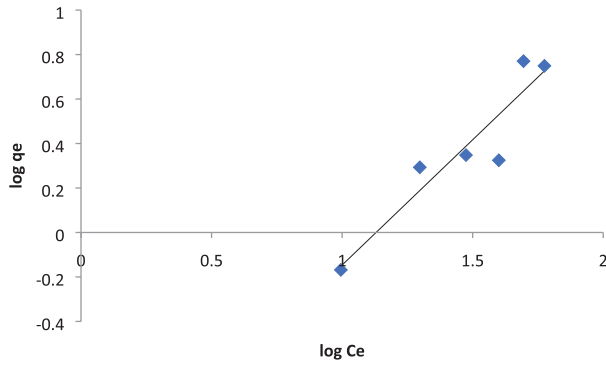
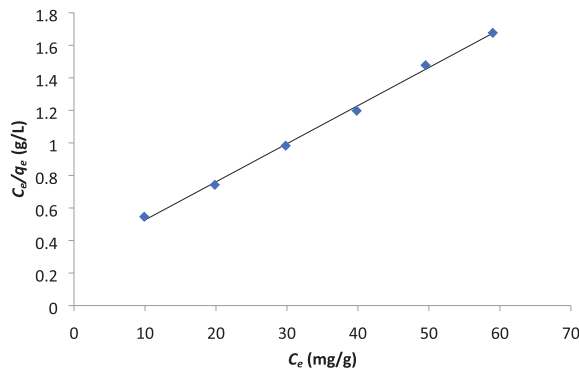**Figure 5.** Freundlich plot of *logq_e* versus *logC_e*.
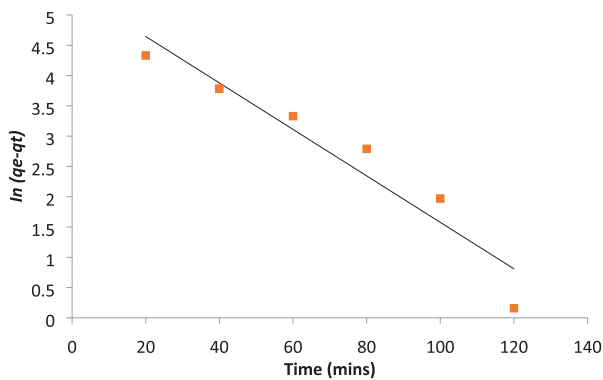

Figure 6. Langmuir plot of C_e/q_e versus C_e.

Figure 7. Pseudo first-order kinetic plots of Cr(VI) sequestration by cMGK-HP.

Figure 8. Pseudo second-order kinetic plots of Cr(VI) sequestration by cMGK-HP.

Figure 9. Plot of ln K_L versus 1/T (K^{-1}) for Cr(VI) sequestration by cMGK-HP at 393–323 K.

against a value of .8941 obtained for pseudo first order kinetic model. The results presented by Parlayici and Pehlivan[31] and Basnet et al[10] were similar to those obtained in this study.

The change in standard enthalpy (ΔH°) and standard entropy (ΔS°) were determined as the respective slope and intercept via plotting *ln K_L* against *1/T* (Figure 9) using equation (9). These values were substituted into equation (10) at different temperatures to estimate the values of ΔG° (change in standard Gibbs free energy) stated in Table 4. The result suggested adsorption to be spontaneous and exothermic (ΔH° and ΔG° were negative), occur by physisorption (ΔG° values range) and possess high degree of disorderliness (ΔS° was positive).

$$InK_L = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \qquad (9)$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad (10)$$

Where R = 8.314 Jmol^{-1}K^{-1} (universal gas constant), K_L = Langmuir constant due to binding sites affinity and adsorption energy and T (°K) = absolute temperature.

Regeneration and reusability of cMGK-HP

The percentage of Cr(VI) removed decreased as the number of adsorption-desorption cycle was increased as depicted in Figure 10. The percentage of Cr(VI) removed from solution

$$In\left(q_e - q_t\right) = Inq_e - k_1 t \qquad (7)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (8)$$

where q_e = equilibrium experimental adsorption capacity (mg g^{-1}), q_e = adsorption capacity at time t (mg g^{-1}), k_1 = pseudofirst-order rate constant (min^{-1}) and k_2 = pseudosecond-order rate constant (g mg^{-1} min^{-1}).

Figures 7 and 8 represent the plots of *ln(q_t-q_e)* versus *t* (pseudo first-order kinetic) and *t/q_t* versus *t* (pseudo second-order kinetic) respectively. A correlation coefficient (R^2) of .9989 obtained for pseudo second order kinetic model suggested its fitness for Cr(VI) removal using cMGK-HP as
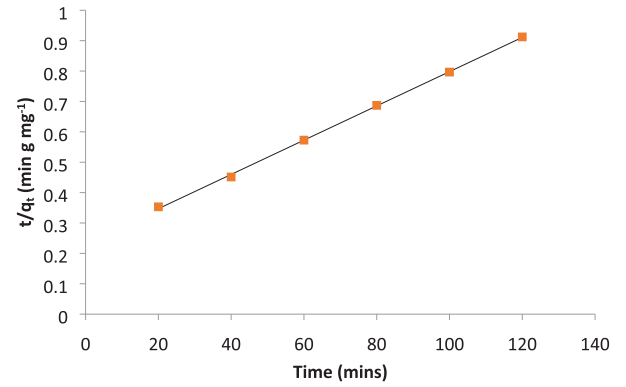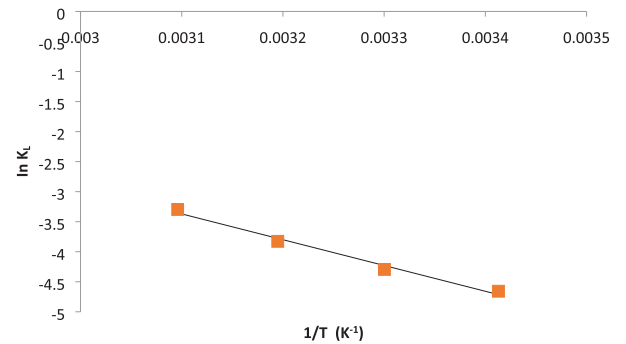
Table 4. Thermodynamic parameters for Cr(VI) sequestration from solution by cMGK-HP.

	ΔS° (J/MOL K)	ΔH° (KJ/MOL)	R^2	ΔG° (KJ/MOL)			
				293 K	303 K	313 K	323 K
cMGK-HP	+34.91	−27.66	0.9985	−37.89	−38.24	−38.59	−38.94
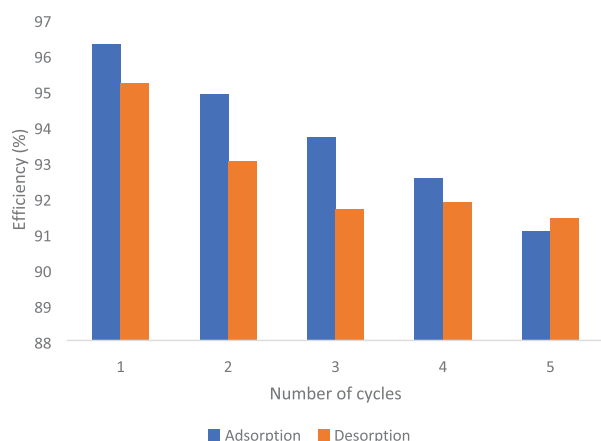
Figure 10. Cr(VI) Adsorption-desorption efficiency after 5 cycles using cMGK-HP.

decreased from 96.29% to 91.05% after the fifth regeneration of cMGK-HP. This resulted from the reduction in the number of active sites on adsorbent surface during dissolution. The result suggests cMGK-HP could be used repeatedly for Cr(VI) sequestration from solution. After the fifth cycle, the percentage removal was greater than 90%.

Clean disposal of effluent and spent adsorbent

In this study, optimum removal of Cr(VI) from solution by cMGK-HP as shown by Taguchi was observed at a pH of 2 signifying a highly acidic condition which makes both the spent adsorbent and filtrate solution to be unsafe for disposal into open environment. These may leach into the soil and disrupt the ecosystem. Thus, the spent Cr(VI)-loaded cMGK-HP was incinerated for 6 hours at a temperature range 680°C to 700°C in a muffle furnace to get the ash, and a solid-liquid ratio of 1:5 was obtained by dissolving 5 mg of the spent adsorbent in 25 mL of deionized water.[32] After stirring for 24 hours, the mixture was then filtered and Cr(VI) concentration was analyzed using atomic absorption spectrophotometer. Absence of Cr(VI) was noticed in the filtrate which signifies the effectiveness of the thermal treatment. The same process was repeated for the sediment obtained in the filtrate after the sequestration. The filtrate was first heated in an oven at a temperature of 120°C for 5 hours to remove the aqueous content. The ash product can be used to keep harmful bugs away at home, add traction to slippery walkways and soak up driveway spills.

Cost implication of Cr(VI) sequestration from solution by cMGK-HP

The high medicinal purpose of *Garcinia kola* has increased its demand by consumers and its marketing efficiency was estimated to be 1.19% indicating that for every unit cost incurred, the value added by marketing is 0.0119.[33] The hulls of *Garcinia kola* generated have been influenced by this value thereby, causing environmental pollution. This could be converted into an effective adsorbent for sequestration of harmful pollutants (such as Cr(VI)) from aqueous environment thereby, reducing the menace of solid waste disposal.

For any proposed treatment method such as adsorption of pollutants from aqueous solution, adsorbent cost is a major cost for consideration. Others are based on the operation process which include washing, drying, sieving, stirring, chemical modification, and incineration costs. The basis of calculation is the electrical energy cost incurred during the operations and 1 L of water. In this study, the method proposed by Das and Debnath[34] was used to evaluate the operational cost of Cr(VI) sequestration from solution by cMGK-HP presented in Table 5.

The economic model (equation (11)) proposed by Das and Debnath[34], was used to calculate the total operational cost (T) of using cMGK-HP as adsorbent for Cr(VI) sequestration from solution.

$$T = \left(\frac{A_1}{A_2} \right) + P + B + R \qquad (11)$$

where A_1 = *Adsorbent* price based on local market = 0.135 $/kg, A_2 = *Practical* loading which is a function of Cr(VI) uptake capacity = 0.77, 0.59, 0.42, 0.33, and 0.21 mole of Cr(VI)/kg for the first, second, third, fourth and fifth regeneration cycle, P = Adsorbent preparation cost = 0.411 $/mole, B = Batch adsorption process cost = 0.078 $/mole, and R = Adsorbent regeneration cost = 0.160 $/mole. For the 5 regeneration cycles, total cost was 5 times 0.160 which gives 0.80 $/mol.

Therefore, $T = 0.175 + 0.411 + 0.078 + 0.160 = 0.824$ $/mole Cr(VI) ions.

The operational cost of commercial activated carbon to remove Cr(VI) from solution has been estimated to be 142.15 Rs./g Cr(VI) ions which is equivalent to 90.413 $/mole Cr(VI) ions in 1 L of aqueous solution.[35] The study conducted by Sharma et al[35] applied adsorbents prepared from almond shells, discarded potato and petha via chemical modification with 0.1 N NaOH and 0.1 N H_2SO_4 for Cr(VI) ion removal from

Table 5. Cost estimation of Cr(VI) sequestration from aqueous solution by cMGK-HP.

OPERATIONS	COST INCURRED FOR PROCESS OPERATIONS ($/MOLE)									Σ
	T	W	D	G	SV	SR	CM	IN	PA	
Preparation of Adsorbent (*P*)	0.092	0.015	0.037	0.058	0.019	0.037	0.116	-	0.037	0.411
Batch adsorption process (*B*)	-	-	-	-	-	0.047	-	-	0.031	0.078
Adsorbent Regeneration (*R*)	-	-	-	-	-	0.049	0.019	0.092	-	0.160

Abbreviations: CM, chemical modification; D, drying; G, grinding; IN, incineration; PA, pH adjustment; SR, stirring; SV, sieving; T, transportation; W, washing.
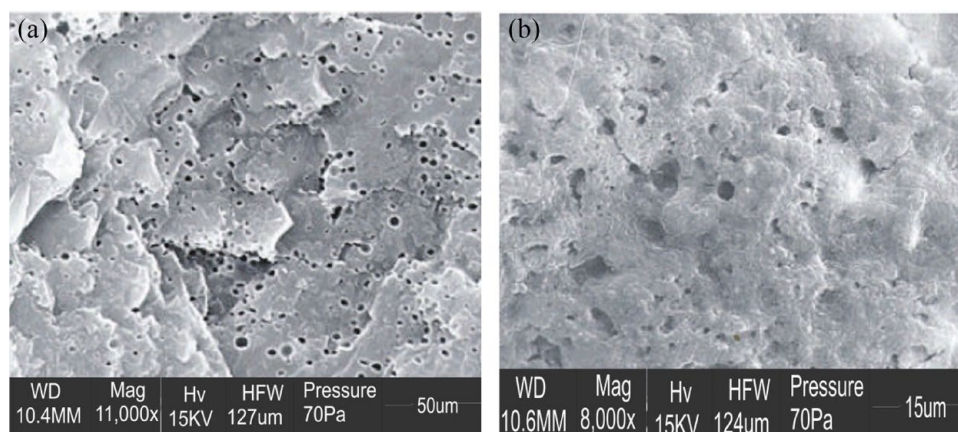

Figure 11. SEM micrograph of cMGK-HP (a) before and (b) after Cr(VI) sequestration.

aqueous solution. The operational cost of Cr(VI) removal from 1 L of aqueous solution using chemically-modified almond shells, discarded potato and petha was estimated to be 6.78 Rs./g Cr(VI) ions, 20.29 Rs./g Cr(VI) ions and 10.99 Rs./g Cr(VI) ions which is equivalent to 4.312 $/mole Cr(VI) ions, 12.905 $/mole Cr(VI) ions and 6.990 $/mole Cr(VI) ions respectively. This suggests that the use of cMGK-HP as adsorbent for Cr(VI) sequestration from solution is less expensive and more economical than previous adsorbents. Rambabu et al[11] revealed a production cost of $1.09/kg using *Phoenix dactylifera* coir biosorbent for hexavalent chromium sequestration and a total cost of $4.36/m³ for scaling up a batch process wastewater treatment plant.

Adsorbent characterization

The surface area, total pore volume and average pore diameter of cMGK-HP were revealed to be 221.75 m²/g, 0.267 cm³/g, and 58.44 Å respectively. The alkaline hydrolysis of raw *Garcinia kola* hull particles with NaOH greatly improved its textural properties when compared with untreated *Garcinia kola* hull particles having surface area, total pore volume and average pore diameter of 52.93 m²/g, 0.092 cm³/g, and 18.11 Å, respectively.

Figure 11 represents the SEM micrographs of cMGK-HP before and after Cr(VI) sequestration from aqueous solution. Figure 11a depicts the surface morphology of cMGK-HP showing formation of more micropores due to chemical
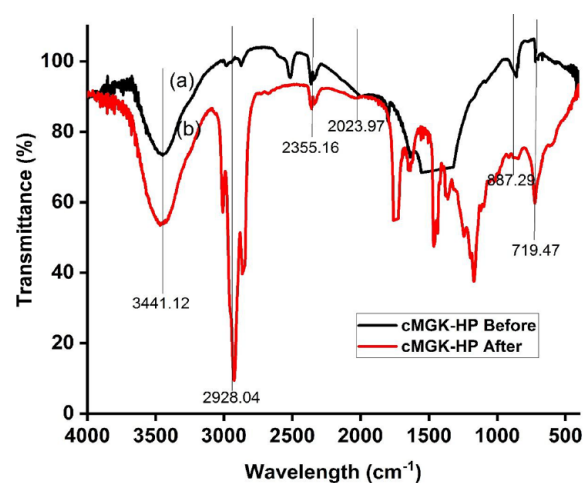
Figure 12. FTIR spectrum of cMGK-HP (a) before and (b) after Cr(VI) sequestration.

modification of the cellulosic compounds present in raw GK-HP. After Cr(VI) sequestration, the number of pores drastically reduced (Figure 11b) as a result of blockage by the Cr(VI) and makes the surface not to be too smooth.

Figure 12a and b represent the FTIR spectra of cMGK-HP before and after Cr(VI) removal. Peaks formed at 3441.12, 2928.04, 2355.16, 2023.97, 887.29, and 719.47 cm⁻¹ in the samples could be attributed to O-H stretching vibration resulting from hydrogen bonding present in cellulose and protein,[36] asymmetric stretching vibration of C-H in methyl group,[37]

strong O=C=O stretching,[6] medium C=C=C stretching,[38] O-Si-O asymmetric stretching[37] and deformation of C-H in cellulose[39] respectively. New peaks were formed at 1462.09 and 1359.86 cm^{-1} on cMGK-HP spectrum after Cr(VI) removal suggesting the occurrence of sequestration.[40]

Mechanism of adsorption

The presence of bending of strong -OH stretching vibration on cMGK-HP surface was shown by FTIR. The surface becomes protonated (positively charged) when the pH is low with the formation of oxy-anions in solution. Adsorption rate is enhanced by the electrostatic attractive forces between (1) hexavalent chromium ions and hydroxyl functional group and (2) hydrogen ions and oxy-anions formed in solution. The adsorbent surface becomes negatively charged at high pH together with the formation of $HCrO_4^-$ and CrO_4^{2-} in solution. Complexes are formed due to the competition of chromium compound oxy-anions with the negative charge which reduces the rate of hexavalent chromium ions removal.

Conclusions

In this study, NaOH-modified *Garcinia kola* hull particles was applied as an adsorbent for Cr(VI) sequestration from solution. Taguchi was used as an optimization tool for the process parameters. The optimum predicted point at pH, contact time, adsorbent dose, Cr(VI) initial concentration and temperature of 2, 20 minutes, 8 g/L, 10 mg/L and 20°C respectively gave 99.02% of Cr(VI) sequestration. The laboratory experiment conducted at this point revealed 98.76% of Cr(VI) sequestration which affirms high significance of the developed mathematical model as shown by ANOVA. The order of parameter contribution to Cr(VI) ion sequestration from solution by cMGK-HP was noticed to be pH > adsorbent dose > initial concentration > contact time > temperature. Experimental data were well-fitted into Langmuir isotherm and pseudo second order kinetic models. Adsorption nature was spontaneous, exothermic, physisorption and possessed high degree of disorderliness. A maximum adsorption capacity of 217.39 mg g^{-1} was obtained for cMGK-HP. Cost analysis revealed using cMGK-HP to be cost effective for Cr(VI) sequestration with a total operational cost of 0.824 \$/mole Cr(VI) ions. The adsorbent possess excellent textural, morphological and active functional groups which made it suitable for hexavalent chromium sequestration from aqueous solution. This will ameliorate environmental challenges that are usually being encountered due to hexavalent chromium pollution of water bodies.

Acknowledgements

Authors' contributions

This declaration is not applicable.

Data availability statement

The data used to support the findings of this study are included within the article.

Ethical approval

This declaration is not applicable.

ORCID iD

Lekan Taofeek Popoola [iD] https://orcid.org/0000-0001-7778-960X

REFERENCES

1. Guo X, Liu A, Lu J, et al. Adsorption mechanism of hexavalent chromium on biochar: kinetic, thermodynamic and characterization studies. *ACS Omega*. 2020;5:27323-27331.
2. Gheju M, Balcu I. Removal of chromium from Cr(VI) polluted wastewaters by reduction with scrap iron and subsequent precipitation of resulted cations. *J Hazard Mater*. 2011;196:131-138.
3. Nag S, Mondal A, Bar N, Das SK. Biosorption of chromium (VI) from aqueous solutions and ANN modelling. *Environ Sci Pollut Res*. 2017;24:18817-18835.
4. Ozsin G, Kılıç M, Apaydın E, Ays V, Pütün E. Chemically activated carbon production from agricultural waste of chickpea and its application for heavy metal adsorption: Equilibrium, kinetic and thermodynamic studies. *Appl Water Sci*. 2019;9:56.
5. Karri RR, Sahu JN, Meikap BC. Improving efficacy of Cr (VI) adsorption process on sustainable adsorbent derived from waste biomass (sugarcane bagasse) with help of ant colony optimization. *Ind Crops Prod*. 2020;143:111927.
6. Popoola LT. Tetracycline and sulfamethoxazole adsorption onto nanomagnetic walnut shell-rice husk: isotherm, kinetic, mechanistic and thermodynamic studies. *Int J Environ Anal Chem*. 2020;100:1021-1043.
7. Sarkar S, Bar N, Das SK. Cr(VI) and Cu(II) removal from aqueous solution in fixed bed column using rice bran: Experimental, statistical and GA modelling. *J Indian Chem Soc*. 2021;98:100216.
8. Liu Q, Li Y, Chen H, et al. Superior adsorption capacity of functionalised straw adsorbent for dyes and heavy-metal ions. *J Hazard Mater*. 2020;382:121040.
9. Yusuff AS, Lala MA, Thompson-Yusuff KA, Babatunde EO. ZnCl$_2$-modified eucalyptus bark biochar as adsorbent: preparation, characterization and its application in adsorption of Cr(VI) from aqueous solutions. *S Afr J Chem Eng*. 2022;42:138-145.
10. Basnet P, Ojha PK, Gyawali D, Ghimire KN, Paudyal H. Thermochemical study of Cr(VI) sequestration onto chemically modified Areca catechu and its recovery by desorptive precipitation method. *Heliyon*. 2022;8:e10305.
11. Rambabu K, Thanigaivelan A, Bharath G, Sivarajasekar N, Banat F, Show PL. Biosorption potential of *Phoenix dactylifera* coir wastes for toxic hexavalent chromium sequestration. *Chemosphere*. 2021;268:128809.
12. Bharath G, Hai A, Rambabu K, Savariraj D, Ibrahim Y, Banat F. The fabrication of activated carbon and metal-carbide 2D framework-based asymmetric electrodes for the capacitive deionization of Cr(VI) ions toward industrial wastewater remediation. *Environ Sci Water Res Technol*. 2020;6:351-361.
13. Bashir S, Zhu J, Fu Q, Hu H. Comparing the adsorption mechanism of Cd by rice straw pristine and KOH-modified biochar. *Environ Sci Pollut Res*. 2018;25:11875-11883.
14. Ghosh K, Bar N, Biswas AB, Das SK. Elimination of crystal violet from synthetic medium by adsorption using unmodified and acid-modified eucalyptus leaves with MPR and GA application. *Sustain Chem Pharm*. 2021;19:100370.
15. Yusuff AS, Ajayi OA, Popoola LT. Application of Taguchi design approach to parametric optimization of adsorption of crystal violet dye by activated carbon from poultry litter. *Sci Afr*. 2021;13:e00850.
16. Eleyinmi AF, Bressler DC, Amoo IA, Sporns P, Oshodi AA. Chemical composition of bitter cola (*Garcinia kola*) seed and hulls. *Pol J Food Nutr Sci*. 2006;56:395-400.
17. Odebunmi EO, Oluwaniyi OO, Awolola GV, Adediji OD. Proximate and nutritional composition of kola nut (*Cola nitida*), bitter cola (*Garcinia kola*) and alligator pepper (*Afromomummelegueta*). *Afr J Biotechnol*. 2009;8:308-310.
18. Moneim A, Sulieman E. Garcinia Kola (Bitter Kola): chemical composition. In: Mariod A, ed. *Wild Fruits: Composition, Nutritional Value and Products*. Springer;2019:112-131.

19. Azadi A, Ahmadi S. Simultaneous magnetic dispersive micro solid phase extraction of valsartan and atorvastatin using a CMC-coated Fe_3O_4 nanocomposite prior to HPLC-UV detection: multivariate optimization. *New J Chem*. 2019;43:16950-16959.

20. Koorand MB, Eslamnejad A, Safa F. Optimization of captopril electrochemical measurement with Box-Behnken and Taguchi Tests. *J Biochem Tech*. 2018; 2:85-93.

21. Nasseh N, Taghavi L, Barikbin B, Harifi-Mood AR. The removal of Cr(VI) from aqueous solution by almond green hull waste material: kinetic and equilibrium studies. *J Water Reuse Desalination*. 2017;7:449-460.

22. Somyanonthanakun W, Ahmed R, Krongtong V, Thongmee S. Studies on the adsorption of Pb(II) from aqueous solutions using sugarcane bagasse-based modified activated carbon with nitric acid: kinetic, isotherm and desorption. *Chem Phys*. 2023;6:100181.

23. Giri SK, Das NN, Pradhan GC. Synthesis and characterization of magnetite nanoparticles using waste iron ore tailings for adsorptive removal of dyes from aqueous solution. *Colloids Surf A Physicochem Eng Asp*. 2011;389:43-49.

24. Li M, Tang C, Fu S, Tam KC, Zong Y. Cellulose-based aerogel beads for efficient adsorption- reduction- sequestration of Cr(VI). *Int J Biol Macromol*. 2022;216:860-870.

25. Rambabu K, Bharath G, Thanigaivelan A, Das DB, Show PL, Banat F. Augmented biohydrogen production from rice mill wastewater through nano-metal oxides assisted dark fermentation. *Bioresour Technol*. 2021;319:124243.

26. Sureshkumar N, Bhat S, Srinivasan S, et al. Continuous phenol removal using a liquid– solid circulating fluidized bed. *Energies*. 2020;13:3839.

27. Ali A, Saeed K. Decontamination of Cr(VI) and Mn(II) from aqueous media by untreated and chemically treated banana peel: a comparative study. *Desalination Water Treat*. 2015;53:3586-3591.

28. Freundlich HMF. Over the adsorption in solution. *J Phys Chem*. 1906;57: 385-471.

29. Langmuir I. The constitution and fundamental properties of solids and liquids. Part I. *Solids J Am Chem Soc*. 1916;38:2221-2295.

30. Ali A, Saeed K, Mabood F. Removal of chromium (VI) from aqueous medium using chemically modified banana peels as efficient low-cost adsorbent. *Alex Eng J*. 2016;55:2933-2942.

31. Parlayici Ş, Pehlivan E. Comparative study of Cr(VI) removal by bio-waste adsorbents: equilibrium, kinetics and thermodynamic. *J Anal Sci Technol*. 2019; 10:1-8.

32. Mitra T, Bar N, Das SK. Rice husk: Green adsorbent for Pb(II) and Cr(VI) removal from aqueous solution—column study and GA–NN modeling. *SN Appl Sci*. 2019;1:486.

33. Iheke OR, Simonyan JB, Egwuatu EU. Efficiency of bitter kola marketing in Abia State, Nigeria. *Niger Agric J*. 2017;48:180-187.

34. Das P, Debnath A. Fabrication of $MgFe_2O_4$/polyaniline nanocomposite for amputation of methyl red dye from water: isotherm modeling, kinetic and cost analysis. *J Dispers Sci Technol*. 2022. doi:10.1080/01932691.2022.2110110

35. Sharma PK, Ayub S, Shukla BK. 2022) Cost and feasibility analysis of chromium removal from water using agro and horticultural wastes as adsorbents. In: *3rd International Conference on Innovative Technologies for Clean and Sustainable Development*. doi:10.1007/978-3-030-51485-3_30

36. Pal DB, Singh A, Jha JM, et al. Low-cost biochar adsorbents prepared from date and delonix regia seeds for heavy metal sorption. *Bioresour Technol*. 2021;339:125606.

37. Cao JS, Lin JX, Fang F, Zhang MT, Hu ZR. A new absorbent by modifying walnut shell for the removal of anionic dye: kinetic and thermodynamic studies. *Bioresour Technol*. 2014;163:199-205.

38. Haro M, Ruiz B, Andrade M, et al. Dual role of copper on the reactivity of activated carbons from coal and lignocellulosic precursors. *Microporous Mesoporous Mater*. 2012;154:68-73.

39. Abbas AF, Ahmed MJ. Mesoporous activated carbon from date stones (*Phoenix dactylifera* L.) by one-step microwave assisted K_2CO_3 pyrolysis. *J Water Process Eng*. 2016;9:201-207.

40. Nazari G, Abolghasemi H, Esmaieli M. Batch adsorption of cephalexin antibiotic from aqueous solution by walnut shell-based activated carbon. *J Taiwan Inst Chem Eng*. 2016;58:357-365.