Parameter Influence, Characterization and Adsorption Mechanism Studies of Alkaline-Hydrolyzed *Garcinia kola* Hull Particles for Cr(VI) Sequestration

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ABSTRACT: Despite the regulations by The World Health Organization (WHO) on the permissible limit of chromium, many industries still discharge wastewater polluted with chromium into the environment irrationally. This poses a lot of risk to aquatic lives and humans because of its carcinogenic and toxic attributes. Thus, treatment of industrial wastewater polluted with chromium is highly imperative before its disposal. Nonetheless, the hulls generated from *Garcinia kola* in our various farmlands also causes environmental pollution when dumped unknowingly. In this present study, *Garcinia kola* hull particles (GK-HP) was hydrolyzed using NaOH and applied as adsorbent for Cr(VI) sequestration. The raw *Garcinia kola* hull particles (rGK-HP) and modified *Garcinia kola* hull particles (cMGK-HP) were characterized using Brunauer-Emmett-Teller (BET) method, scanning electron microscopy (SEM), powder X-ray diffractometry (XRD), Fourier-Transform-Infrared (FTIR), thermogravimetric analysis (TGA), energy dispersive spectroscopy (EDS) and point of zero charge (pH_{pzc}). The influence of pH, adsorbent dose, contact time, temperature and adsorbate initial concentration on Cr(VI) sequestration were examined. The cMGK-HP was able to remove 96.25% of Cr(VI) from solution and proved to be effective than rGK-HP. The amount of Cr(VI) removed from solution decreased as the pH and adsorbate initial concentration were increased. However, the amount increased as the adsorbent dose, contact time and temperature were increased. Change in morphological structure, textural property, spectral peak, phase composition and adsorbents chemical composition before and after Cr(VI) sequestration from solution were proved by SEM, BET, FTIR, XRD, and EDS analyses respectively. The isotherm and kinetic studies suggest Cr(VI) adsorption on adsorbents' surface to be monolayer in nature and adsorption data to be well-fitted into pseudo second order model respectively. The cMGK-HP possessed excellent reusability attribute and high thermal stability as shown by TGA. In conclusion, cMGK-HP could effectively be used as an adsorbent for Cr(VI) sequestration from solution.

KEYWORDS: *Garcinia kola*, alkaline-hydrolyzed, chromium, regeneration, adsorption mechanism

Introduction

Chromium exists in 2 forms as either trivalent or hexavalent[1] but the latter is more carcinogenic and mutagenic to human beings and animals[2] with toxicity of about 500 times more than the former.[3] Cr(VI) poses threat to ecological environment[4] and human respiratory tract, kidney, liver, immune and gastro-intestinal systems when absorbed into the body system at low concentration.[5] Of all the existing heavy metals, chromium possess oxidation states ranging between –2 and +6[6]; and its carcinogenicity and toxicity mechanisms can cause genomic instability, DNA damage and reactive oxygen species generation in humans.[7] The World Health Organization (WHO) permissible discharge limit for chromium is 0.05 mg/L. However, rapid industrialization and agricultural activities have made the use of Cr(VI) to be unavoidable. Hexavalent chromium is used for different applications in various manufacturing and industrial companies engaged in steel fabrication, electroplating, wood preservatives, paints and pigments, metal finishing, canning, tanneries and many more.[8] Thus, industrial wastewater containing chromium from these industries are irrationally discharged into the environment causing soil and water pollution.[2] Nonetheless, chromium is one of constituents of pesticides which are widely used for agricultural purposes.[9] Chromium-wastewater finds its way through surface runoff into rivers and lakes or via permeation into ground water.[10] Thus, treatment of Cr(VI)-wastewater before discharging is essential to keep our environment safe.

So far, adsorption has been tagged an effective way of remediating and removing Cr(VI) from wastewater among many chemical, biological and physical treatment processes.[11] This is due to its cheap price, better removal efficiency, operation simplicity, low energy consumption, wide availability and many more.[12] The prospects of adsorption application for the removal of chromium from solution had been discussed extensively.[13] Other methods proved to form large quantity of slug, generate secondary waste and have exorbitant operational costs.[14] High cost of commercial activated carbon has stimulated researchers to be using agricultural bye-products and wastes such as palm oil shells,[15] saw dust,[16] coconut shell,[17] sugar cane bagasse,[18] walnut shell,[19] rice husk,[20] soya bean hulls,[21] rice bran,[22] and so on as low cost adsorbents to remove heavy metals from polluted wastewater before discharge. This resulted from their richness in cellulose, lignin, pectin and other useful compounds. Hydroxyl, carbonyl, carboxylic,

amino and alkoxy are the functional groups present in these compounds which make them to have high affinity for metal ions available in wastewater and improve their adsorption efficiencies.[23] Chemically modified adsorbents from agro-wastes usually exhibit higher adsorption capacities than the unmodified adsorbents.[21] This is because pores of cellulose fibers in unmodified adsorbents are often occupied by many viscous compounds such as pectin and lignin.[24]

In previous studies, agrowaste materials such as oak saw dust,[25] magnetic chitosan resins,[26] banana peels[10] and chickpea,[27] rice straw,[28] and biochar[29] were chemically modified and applied for the removal of Cr(VI) from solution. Lakshmi et al[30] immobilized *Aspergillus carbonarius* with the aid of sodium alginate to improve its adsorption capacity for Cr(VI) from electronic waste. The result revealed maximum removal of 92.43% at a pH of 2.0 for 12 hours at 37°C. The study conducted by Imran et al[31] revealed magnetite nanoparticles to be a better activation agent for biochar of *Chenopodium quinoa* crop residues than strong nitric acid for Cr(VI) removal with respective maximum efficiency of 93.62% and 79.8%. Vunain et al[32] removed 99.88% and 99.52% of Cr(VI) ions from solution using rice husk and potato peel respectively activated with phosphoric acid. *Arundo donax* stem modified using sulfuric acid exhibited more than 90% removal for Cr(VI) ions.[33] Vaddi et al[34] used aluminum metal blended with groundnut shell to remove 94.2% of Cr(VI) ion from solution at pH 4.0, initial concentration 100 mg/L, adsorbent dosage 8 g/L and time of 50 minutes. Rai et al[35] modified pomegranate peel with concentrated sulfuric acid and used it as adsorbent for Cr(VI) sequestration from an aqueous solution. A maximum adsorption capacity of 82.99 mg/g was recorded at room temperature with a pH and contact time of 2.0 and 180 minutes respectively. At a pH, contact time, adsorbent dose and initial Cr(VI) concentration of 5, 90 minutes, 2 g and 2.25 mg/L, 98.4% of Cr(VI) was removed from solution using activated carbon prepared from *Eichhornia crassipes* via simultaneous dilute sulfuric acid and thermal activation.[36]

However, information on the application of *Garcinia kola* hull together with its activation via alkaline hydrolysis for the sequestration of Cr(VI) from solution is rare to the best of author's knowledge. This study *uniquely* applied alkaline-hydrolyzed *Garcinia kola* hull particles (cMGK-HP) using sodium hydroxide for Cr(VI) sequestration from solution. The hull is highly rich in protein, fiber and cellulose[37] and also contains bioactive compounds such as flavonoids, alkaloids, tannins, saponins cyanogenic, and glycosides.[38] These make it suitable for use as adsorbent in heavy metals removal from solution. The modification of the hull particles via alkali hydrolysis using sodium hydroxide helps in breaking down long cellulose chains. Also, the reaction between the sodium hydroxide and active functional groups in the pre-hydrolyzed hull particles influences increase in the number of pore openings and surface area available for the Cr(VI) sequestration.[39]

The influence of contact time, pH, adsorbent dose, temperature and initial Cr(VI) concentration on Cr(VI) adsorption from solution was examined. Unmodified and chemically modified adsorbents were characterized before and after the adsorption of Cr(VI) using BET, SEM, XRD, FTIR, TGA, and EDS. Adsorption mechanism was proposed; and adsorbent regeneration and reusability studies were executed.

Methods and Materials

Chemicals and stock solution preparation

The chemicals were analytical grade and used without any alteration. A 1000 mg/L of Cr(VI) stock solution was prepared by dissolving 2.8255 g of $K_2Cr_2O_7$ salt in 1000 mL of distilled water. Various concentrations of Cr(VI) needed for the experimental work were prepared using distilled water to dilute the stock solution. The pH of the solution was controlled using either NaOH or HCl solutions. KNO_3 (0.1 and 0.01 M) was used for point of zero charge analysis.

Adsorbent preparation

Collected hulls of *Garcinia kola* from a local market were thoroughly washed using tap water and rinsed using distilled water to get rid of unwanted materials. Hulls were dried for 7 days under sunlight and dried in an oven for 48 hours at 105°C to remove retained water. The dried hulls were mechanically milled into fine particles and an electric sieve shaker was used to obtain particle size of <150 μm. The hull particles (500 g) were alkali-hydrolyzed in a round bottom flask for 3 hours at 120 rpm under reflux using 500 mL of 10% NaOH. The particles were cooled, filtered, thoroughly washed using distilled water till neutrality and dried for 24 hours in an oven at 105°C. This breaks down the long cellulose chains into smaller monomers and also removes pectin and lignin present. The obtained filtrate was treated with phenolphthalein to know the degree of sample neutrality. During alkaline hydrolysis, a reaction between NaOH and acidic –OH/any free –COOH in the pre-hydrolyzed *Garcinia kola* hull particles (GK-HP) occurs. This forms the chemically-modified *Garcinia kola* hull particles (cMGK-HP) used in this study and also develops suitable complexation sites for Cr(VI) removal present in solution. The untreated (raw) *Garcinia kola* hull particles (rGK-HP) was also simultaneously kept in a tight nylon and desiccator for comparison purpose.

Characterization of adsorbent

Effect of chemical modification on textural characteristics of cMGK-HP was studied by Brunauer-Emmett-Teller method with the aid of Quantachrome Autosorb instrument (Nova 11.03A, USA version). Examination of adsorbent elemental composition and structural morphology was achieved via

scanning electron microscope (SEM/EDX-JEOL-JSM 7600F). The phase composition of chemically modified GK-HP was studied using powder X-ray diffractometer (Rigaku D/Max-III, Tokyo, Japan). Several functional groups present in rGK-HP and cMGK-HP were detected via FTIR spectrometer (Nicolet iS10 FT-IR Spectrometer). TGA analyzer (PerkinElmer; analysis condition: heating rate = 30°C min^{-1}, N$_2$ carrier flow rate = 20 mL min^{-1} and temperature range = 30°C-800°C) was used to detect thermal decomposition trend. Point of zero charge analysis was executed to examine the chemical modification effect on the surface charges of the adsorbents.

Process parameter influence

The influence of pH (2-12), contact time (20-120 minutes), adsorbent dose (2-12 g/L), Cr(VI) initial concentration (10-60 mg/L) and temperature (20°C-60°C) were investigated. The adsorbent, in specified quantity, was reacted with 50 mL of Cr(VI) salt solutions in a 250-mL flask for batch experiments. The flask was placed on a heater (temperature-controlled) operated at 160 rpm, specified temperature and time. The filtrate and the residue were separated using Whatman filter paper. Cr(VI) concentration was determined by preparing a standard solution of 1,5-diphenylcarbazide in acetone and Atomic Adsorption Spectrophotometer (Buck scientific model 210 VGP) was used at maximum wavelength (λ_{max}) of 540 nm. Percentage of Cr(VI) removed from solution (X, %) and sorption capacity of GK-HP (q_e, mg/g) were determined using equations (1) and (2) respectively.

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

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

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

Regeneration and reusability of cMGK-HP

Consecutive adsorption-desorption experiments were done to substantiate the reusability capacity of cMGK-HP for Cr(VI) sorption. The first adsorption experiment was conducted via the addition of 0.5 g Cr(VI) ions loaded cMGK-HP to 50 mL of 0.1 M HNO$_3$ solution in a conical flask (operated at 80°C and stirred for 2 hours). This enhances the oxygen-containing functional groups present in the regenerated adsorbent.[40] After this, cMGK-HP was washed thoroughly using distilled water at 7.0 pH, dried for 6 hours at 80°C and reused consecutively for 5 times. Desorption efficiency was calculated using the method prescribed by Giri et al.[41]

Discussion of Results

Characterization

Brunauer–Emmett–Teller analysis. The BET results revealed the surface area, total pore volume and average pore diameter of cMGK-HP to be 221.75 m^2/g, 0.267 cm^3/g, and 58.44 Å respectively. The values obtained are closer to those presented by Yusuff et al[29] in which ZnCl$_2$-modified eucalyptus bark biochar was used for the removal of Cr(VI) from solution. Nonetheless, chemical modification of raw *Garcinia kola* hull particles via alkaline hydrolysis 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 m^2/g, 0.092 cm^3/g, and 18.11 Å respectively.

Scanning electron microscopy analysis. The SEM micrographs of rGK-HP and cMGK-HP before and after Cr(VI) sequestration from aqueous solution are presented in Figure 1. The image depicts presence of few micropores on rGK-HP surface which is unevenly distributed and rough in nature (Figure 1a). The pores were filled up and blocked with Cr(VI) after sequestration and makes the surface to be relatively smooth (Figure 1b). Figure 1c depicts the surface morphology of cMGK-HP showing formation of more micropores due to chemical modification of the cellulosic compounds present in raw GK-HP. After Cr(VI) sequestration, the number of pores drastically reduced (Figure 1d) as a result of blockage by the Cr(VI) and makes the surface not to be too smooth. In all the examined adsorbents, the particle size ranges between 10 and 50 μm. Similar result was presented by Ali et al[42] using raw and NaOH-modified banana peels for Cr(VI) sequestration.

Powder X-ray diffractometer analyses. The XRD patterns of rGK-HP and cMGK-HP at 2θ value between 0 to 70° are shown as Figure 2. In both, peaks of Quartz [2θ (27°, 50°, and 68°)], Calcite [2θ (30°, 47°, and 49°)] and Chlorite [2θ (5°, 13°, and 60°)] were predominant. However, peaks transformation of Berlinite [2θ (26° and 68°)] and Sepiolite [2θ (8°, 20°, and 37°)] in rGK-HP (Figure 2a) to Gypsum [2θ (30° and 50°)] and Sodalite [2θ (15° and 25°)] in cMGK-HP (Figure 2b) occurred due to the chemical modification via NaOH hydrolysis.

Fourier-transform-infrared analyses. The FTIR spectra of rGK-HP (Figure 3a), prepared cMGK-HP (Figure 3b) and used cMGK-HP after Cr(VI) removal (Figure 3c) are presented. 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,[43] asymmetric stretching vibration of C-H in methyl group,[44] strong O=C=O stretching,[20] medium C=C=C stretching,[45] O-Si-O asymmetric stretching[44] and deformation of C-H in cellulose[46] respectively.
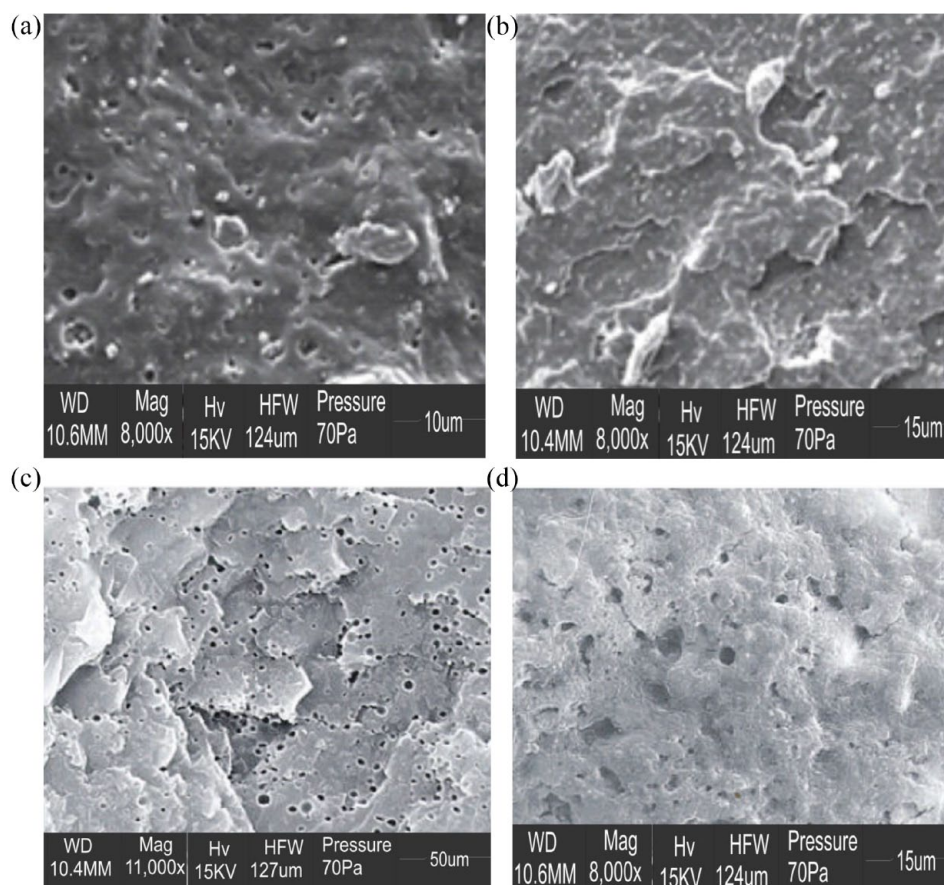
Figure 1. SEM micrograph of rGK-HP (a) before and (b) after Cr(VI) sequestration; and cMGK-HP (c) before and (d) after Cr(VI) sequestration at Cr(VI) initial concentration.

However, peak formed at 2521.05 cm⁻¹ on rGK-HP spectrum disappeared after the chemical modification. Also, new peaks were formed at 1462.09 and 1359.86 cm⁻¹ on used cMGK-HP spectrum. These observations indicate the significance of chemical modification of the rGK-HP using NaOH and Cr(VI) sequestration by cMGK-HP.[47]

Thermogravimetric analyses. The TGA analyses of rGK-HP and cMGK-HP followed similar trend (Figure 4) but exhibited different weight loss characteristics due to the chemical modification. Loss in weight of 6.8% (rGK-HP) and 6.1% (cMGK-HP) were observed at 49.3°C due to evaporation of water. The second stage involves decomposition of protein and occurred at 267.9°C.[48] At this point, rGK-HP and cMGK-HP lost 37.4 and 29.2% of their weight. Weight loss of 56.4% (rGK-HP) and 37.7% (cMGK-HP) were noticed at the third stage. This was noticed at 369.6°C as a result of cellulosic material decomposition in the adsorbents.[49] A relatively constant weight loss was observed for both adsorbents at the final stage. Finally, rGK-HP and cMGK-HP were able to retain 30.17 and 44.1% of their respective weight at 700°C. The hydrolysis of cMGK-HP using NaOH made it to have better thermal stability than rGK-HP. Similar trend was noticed in the result of Derdour et al[50] where both raw and iron-modified

walnut shell were used as adsorbents for hexavalent chromium removal from wastewater.

Energy dispersive spectroscopy analyses. The results of EDS analyses for rGK-HP and cMGK-HP before and after Cr(VI) sequestration are presented in Table 1. The elemental compositions of adsorbents are presented in weight %. Presence of Ca, Si, Al, C, S, K, Na, Mg, H, and O were noticed with different weight % in both adsorbents before Cr(VI) sequestration. However, the weight % of Na, H and O was higher in cMGK-HP due to the reaction between NaOH and acidic –OH/any free –COOH in pre-hydrolyzed *Garcinia kola* hull particles during hydrolysis using NaOH. Generally, variations in the elemental compositions of rGK-HP and cMGK-HP could be linked to the chemical modifications of the protein, fiber and cellulose present in raw *Garcinia kola* hull particles.[51] Nonetheless, presence of Cr was noticed in both adsorbents after the removal due to Cr(VI) sequestration by the adsorbent particles. However, cMGK-HP recorded higher Cr composition (9.27 wt%) than rGK-HP (3.93 wt%) resulting from improvement in surface area, creation of additional pores and presence of active functional groups as evident in earlier presented SEM, BET and FTIR results due to NaOH hydrolysis. This enables cMGK-HP to have better affinity for Cr(VI) removal from
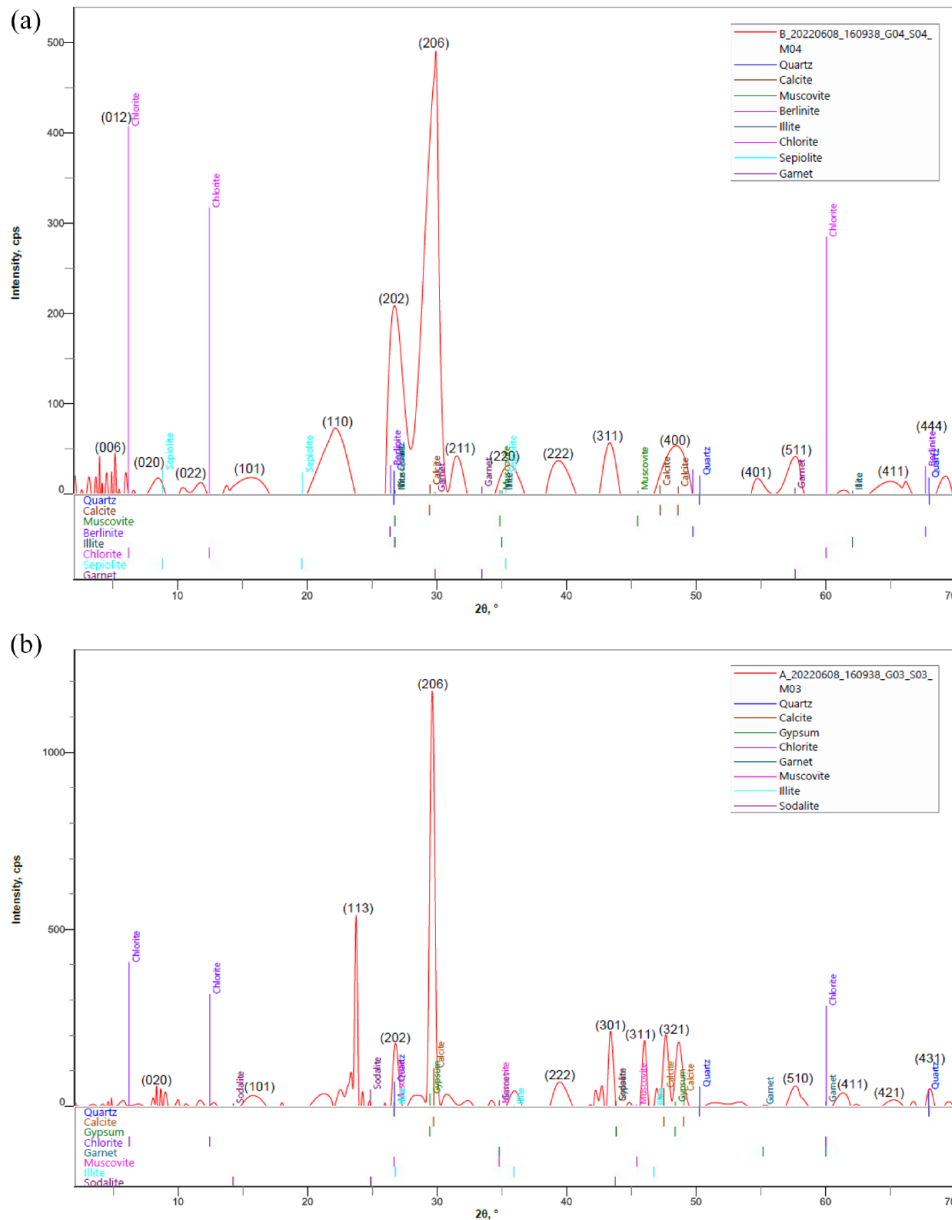
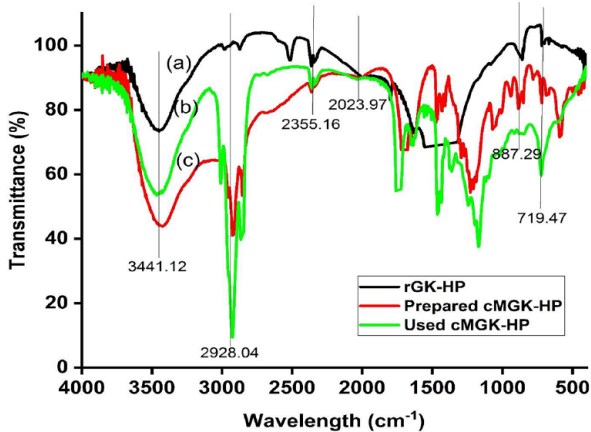**Figure 2.** Powder-XRD spectrum of (a) rGK-HP and (b) cMGK-HP.

Figure 3. FTIR spectrum of prepared (a) rGK-HP, (b) prepared cMGK-HP and (c) used cMGK-HP after Cr(VI) sequestration.

solution. The other elements present have the potential to form ionic bonds in solution to produce hydroxides which enhances the forces of attraction between the adsorbent and the Cr(VI) in solution thereby, improving the adsorbent affinity for Cr(VI) removal.

Point of zero charge (pH_{pzc}) analysis. The ionic state of both rGK-HP and cMGK-HP was determined by measuring the pH at point of zero charge (pH_{pzc}) using the prescribed method by Singha and Das[52] and Banerjee et al[53]. The surface of the adsorbent becomes neutral at pH_{pzc}. Different conical flasks, each containing 30 mL of 0.01 and 0.1 M potassium nitrate having different pH ranging 3 to 10 were prepared. For each of the molar solution, 0.2 g of rGK-HP and cMGK-HP was added and equilibrated for a day. Then, measurement was taken for the pH of supernatant solutions. The value of pH_{pzc} was
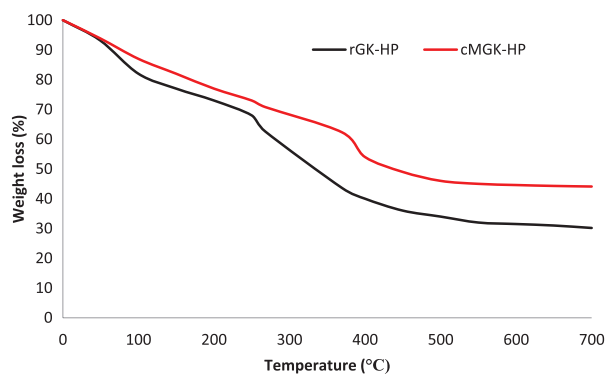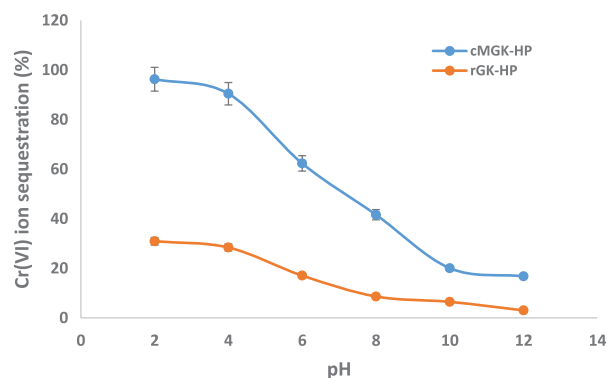
Figure 4. TGA of rGK-HP and cMGK-HP.

Table 1. EDS of rGK-HP and cMGK-HP before and after Cr(VI) sequestration.

ELEMENT	BEFORE SEQUESTRATION (WT %)		AFTER SEQUESTRATION (WT %)	
	RGK-HP	CMGK-HP	RGK-HP	CMGK-HP
Ca	12.16	13.67	12.32	12.77
Si	22.59	21.76	23.11	19.52
Al	2.46	1.48	3.52	3.14
C	12.77	4.55	10.35	3.11
S	2.18	1.05	3.62	1.35
K	6.99	6.24	6.44	6.52
Na	2.36	11.74	2.16	8.48
Mg	9.23	4.8	9.2	3.87
H	12.51	14.56	11.04	13.63
O	16.75	20.15	14.39	18.34
Cr	ND	ND	3.85	9.27

recorded at the intersection point between the initial pH and pH difference. Chemical modification effect of rGK-HP was observed. The pH_{pzc} reduced from 6.29 to 2.41 which suggests that cMGK-HP has several functional groups which are acidic in nature. Thus, the surface of cMGK-HP becomes positively charged when $pH < pH_{pzc}$ which is suitable for Cr(VI) anions sequestration from solution and vice versa when $pH > pH_{pzc}$. At this point, the attractive force between cMGK-HP surface (negatively charged) and Cr(VI) cations is increased which makes its sequestration to be favorable. A reduction in cMGK-HP adsorption efficiency with alkaline solution is acceptable for the observed pH_{pzc}.

Process parameter influence

Effect of Ph. Adsorption of chromium is greatly affected by aqueous solution pH. It has significant effects on Cr(VI) speciation and ionization degree as well as adsorbent surface
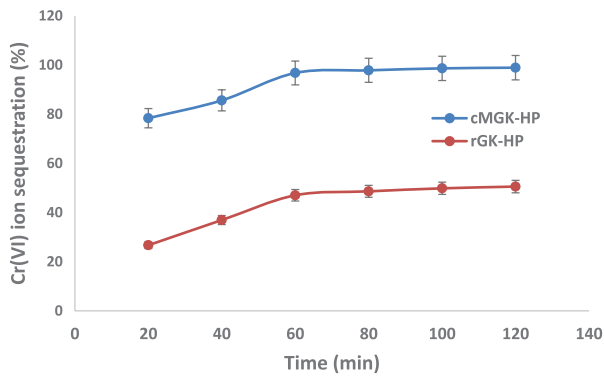

Figure 5. The influence of pH on Cr(VI) ion sequestration using rGK-HP and cMGK-HP. Temperature: 40°C; stirring rate: 120 rpm; solution volume: 50 mL; adsorbent dose: 8 g/L, contact time: 60 minutes; Cr(VI) initial concentration: 20 mg/L.
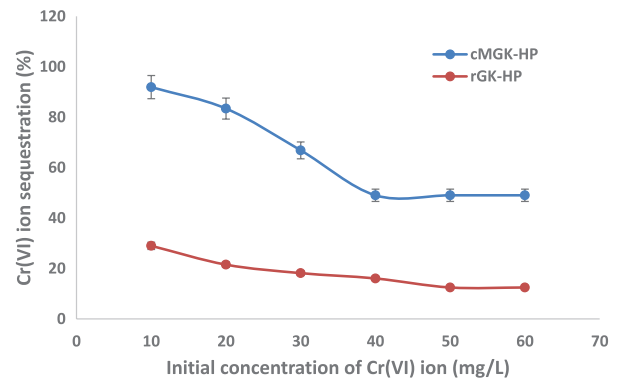
charge.[54] The increase in solution pH from 2.0 to 12.0 significantly decreased the Cr(VI) ion removed from solution from 30.91 ± 0.43 to $3.02 \pm 0.11\%$; and 96.25 ± 0.51 to $16.77 \pm 0.59\%$ for rGK-HP and cMGK-HP respectively (Figure 5). Solutions pH was adjusted via 0.1 M HCl and 0.1 M NaOH. Though maximum Cr(VI) ion sequestration was obtained at optimum pH of 2 for both rGK-HP and cMGK-HP, alkaline hydrolysis of rGK-HP significantly enhanced creation of more complexation sites for Cr(VI) removal. All further experiments were executed at this optimum pH. Similar results were reported using chemically modified almond green hull waste material[55] and *Areca catechu*.[56]

The existence of Cr(VI) in solution is the form of $Cr_2O_7^{2-}$ and $HCrO_4^-$ at the optimum pH for its adsorption. At acidic pH, the dominant form is $HCrO_4^-$ which is released as a result of dichromate ion $Cr_2O_7^{2-}$ hydrolysis. Highly protonated adsorbents surface favors Cr(VI) removal in this predominant anionic form which increases the amount removed from solution. As the pH deviates from acidic to basic, increase in the effluent concentration of $Cr_2O_7^{2-}$ becomes noticeable. At this point, active sites dissociation occurs on adsorbents surface and makes it to be negatively charged. This makes complexation of negatively charged Cr(VI) anions difficult (due to repulsive forces) and thus, reduction in the percentage of Cr(VI) sequestration was noticed.
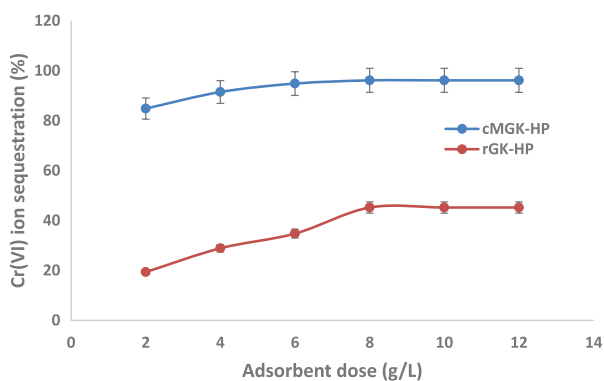
Effect of contact time. Cr(VI) ion percentage removed from solution increased from $26.71 \pm 0.27\%$ to $50.55 \pm 0.59\%$; and $78.38 \pm 0.28\%$ to $98.91 \pm 0.44\%$ as the contact time was increased from 20 to 120 minutes for rGK-HP and cMGK-HP respectively (Figure 6). Higher removal of Cr(VI) ion by cMGK-HP could be linked to increase in adsorbent active sites number due to the chemical modification of rGK-HP. However, optimum adsorption equilibrium time was reached by both adsorbents at 60 minutes. Before this time, bulk of adsorption was noticed due to higher forces of attraction within the active sites on adsorbents' surface and the Cr(VI) ions. No significant change was noticed in the equilibrium

Figure 6. The influence of contact time on Cr(VI) ion sequestration using rGK-HP and cMGK-HP. Temperature: 40°C; stirring rate: 120 rpm; solution volume: 50 mL; adsorbent dose: 8 g/L; pH: 2; Cr(VI) initial concentration: 20 mg/L.

Figure 7. The influence of adsorbent dosage on Cr(VI) ion sequestration using rGK-HP and cMGK-HP. Temperature: 40°C; stirring rate: 120 rpm; solution volume: 50 mL; contact time: 60 minutes; pH: 2; Cr(VI) initial concentration: 20 mg/L.

concentration with further increase in the reaction time from 60 to 120 minutes. Within this period, equilibrium was attained and there was limitation in the number of adsorbents' active sites. At this point, the sequestration rate is a function of Cr(VI) transportation rate from the external to the internal sites of rGK-HP and cMGK-HP. This makes intraparticle diffusion process to dominate over adsorption. Similar findings were reported in previous studies.[56]

Effect of adsorbent dosage. The study of adsorbent dosage effect also revealed high significance of alkaline hydrolysis of the raw GK-HP on the Cr(VI) ion sequestration from solution. The percentage of Cr(VI) ion removed by cMGK-HP was higher than rGK-HP. As the adsorbent dose was increased from 2 to 12 g/L, the percentage of Cr(VI) ion removed from solution increased from 19.33 ± 0.12 to $45.18 \pm 1.06\%$; and 84.81 ± 0.73 to $96.25 \pm 0.72\%$ for rGK-HP and cMGK-HP respectively (Figure 7). Increasing adsorbent dosage causes increase in active sites number present on adsorbent surface. However, above adsorbent dosage of 8 g/L, equilibrium was attained with no significant Cr(VI) removal. This was due to the saturation of the active sites available. The result obtained was analogous

Figure 8. The influence of Cr(VI) initial concentration on its percentage removal from solution using rGK-HP and cMGK-HP. Temperature: 40°C; stirring rate: 120 rpm; solution volume: 50 mL; contact time: 60 minutes; pH: 2; adsorbent dosage: 8 g/L.

to those of Mandina et al[57] and Khan et al[58] where chemically modified orange peel and guar gum-nano zinc oxide were used for hexavalent chromium removal from solution respectively.
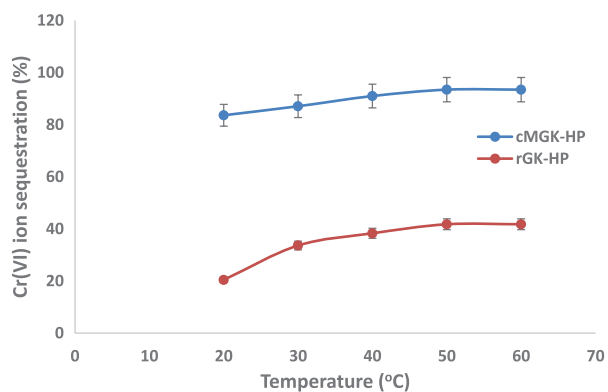
Effect of Cr(VI) ion initial concentration. According to Figure 8, Cr(VI) ion percentage removal from solution decreased from $28.99 \pm 1.02\%$ to $12.48 \pm 0.99\%$ and $91.91 \pm 0.58\%$ to $49.03 \pm 0.88\%$ using rGK-HP and cMGK-HP respectively at a constant dosage of 8 g/L. This observation could be linked to reduction in active sites number available on adsorbents surface as Cr(VI) ion initial concentration was increased. Constant percentage of Cr(VI) ion removal was attained after 50 and 40 mg/L of Cr(VI) ion for rGK-HP and cMGK-HP respectively. At these points, the adsorbent surface is highly saturated and further increase in Cr(VI) ion initial concentration has no significant effect on its percentage removal. This observation is in line with the results presented by Ali and Saeed[10] in which unmodified and chemically modified banana peel were applied for the decontamination of Cr(VI) polluted water. Similarly, the report by Nasseh et al[55] revealed decrease in the percentage removal of Cr(VI) from solution with increasing pollutant concentration using almond green hull as adsorbent.

Effect of temperature. As shown in Figure 9, as the temperature was increased from 20°C to 60°C, the percentage of Cr(VI) ion sequestration increased from $20.41 \pm 0.07\%$ to $41.75 \pm 0.82\%$ and $83.58 \pm 0.93\%$ to $93.42 \pm 0.70\%$ using rGK-HP and cMGK-HP respectively. These results could be linked to increase in the temperature acting as the driving force enhancing the transition of adsorbent particles.[59]

Isotherm, Kinetics and thermodynamics investigation

Isotherm study. Equations 3 and 4 stand for the linearized forms of Freundlich[60] and Langmuir[61] models used for the isotherm study. The linear plots of Freundlich (Figure 10) and Langmuir (Figure 11) are presented. For the Freundlich plot,
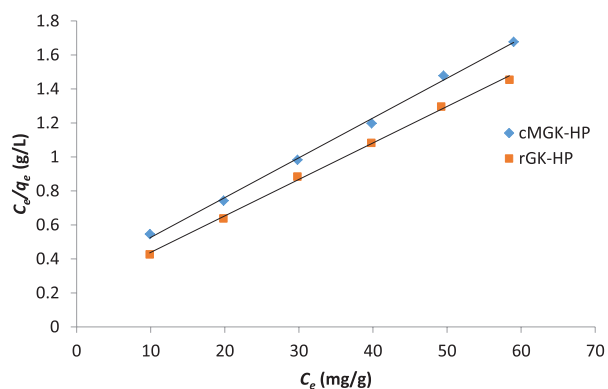
Figure 9. The influence of temperature on the percentage removal of Cr(VI) ion from solution by rGK-HP and cMGK-HP. Cr(VI) initial concentration: 20 mg/L; stirring rate: 120 rpm; solution volume: 50 mL; contact time: 60 minutes; pH: 2; adsorbent dosage: 8 g/L.
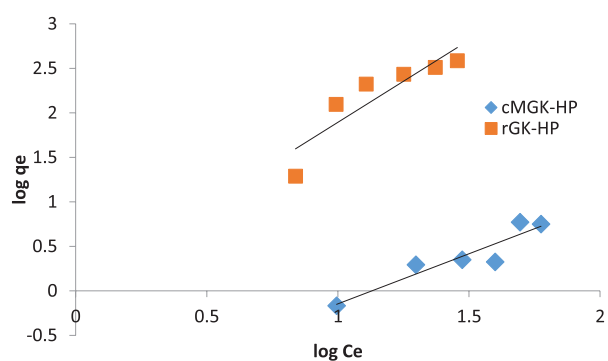

Figure 10. Freundlich plot of $log\ q_e$ versus $log\ C_e$.

Figure 11. Langmuir plot of C_e/q_e versus C_e.

R^2 values of .8048 and .8780 were obtained for rGK-HP and cMGK-HP respectively. For the Langmuir plot, R^2 values of .9915 and .9984 were respectively obtained for rGK-HP and cMGK-HP as adsorbents for the Cr(VI) removal. This indicates the fitness of Langmuir isotherm to represent the adsorption data due to the closeness of its R^2 values to unity. Hence, monolayer adsorption of Cr(VI) on adsorbents' surface is suggested. Maximum adsorption capacities of 60.24 mg g^{-1} and 217.39 mg g^{-1} were recorded for rGK-HP and cMGK-HP respectively. The summary of the result of isotherm study is
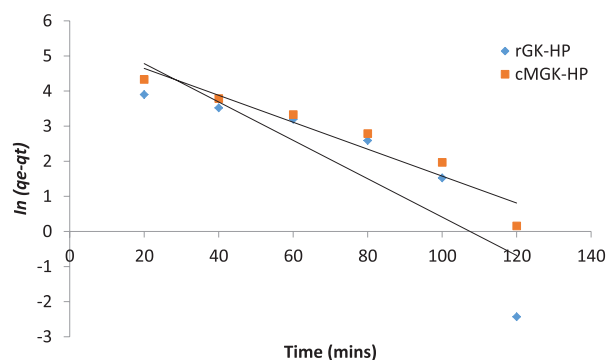
Figure 12. Pseudo first-order kinetic plots.

Table 2. The summary of isotherm models result.

ISOTHERM MODELS	RESULTS	
	RGK-HP	CMGK-HP
Freundlich		
K_F	1.1205	0.0533
n	1.8622	2.7248
R^2	0.8048	0.8780
Langmuir		
K_L	0.0572	0.0158
R_L	0.6362	0.8633
q_{max}	60.24	217.39
R^2	0.9915	0.9984

presented in Table 2. Table 3 presents the adsorption capacities of previously used adsorbents for Cr(VI) removal. This indicates the effectiveness of the particles from *Garcinia kola* hull and its alkaline hydrolyzed form to be excellent adsorbents for Cr(VI) ions.

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{3}$$

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}}\frac{C_e}{q_{max}} \tag{4}$$

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 (L mg^{-1}) and q_{max} = Langmuir maximum adsorption capacity (mg g^{-1}).

Kinetic study. The linearized pseudo first-order and pseudo second-order kinetic models are respectively stated as Equations 5 and 6. The kinetic parameters obtained for the plots of $ln(q_t-q_e)$ against t (Figure 12) and t/q_t against t (Figure 13) are

Table 3. Adsorption capacities of previously used adsorbents for Cr(VI) removal.

ADSORBENT	ADSORPTION CAPACITY (MG/G)	PERCENTAGE REMOVAL (%)	REFERENCE
Almond green hull powder	10.123	99.94	Nasseh et al[55]
Walnut shell-Fe	29.67	-	Derdour et al[50]
Peanut shell Almond shell Walnut shell	22.94 24.25 24.52	87.8 90.2 92.2	Das et al[62]
Rice husk	10.18	85.5 –98.5	Mitra et al[63]
$MnFe_2O_4$-/polyaniline nanocomposite	175.44	99.01	Das et al[64]
Heinsia crinita seed coat	231.7	>90%	Dawodu et al[65]
$ZnCl_2$-Eucalyptus bark biochar	36.18	94.47	Yusuff et al[29]
Chemically modified dormant *Aspergillus niger* spores	177	91	Ren et al[66]
$CaFe_2O_4/ZrO_2$ -MNC	178.57	95	Bhowmik et al[67]
Arundo donax stem	76.92	>90	Bhattarai et al[33]
Al embedded groundnut shell	13.458	94.2	Vaddi et al[34]
Eichhornia crassipes	-	98.4	Fito et al[36]
rGK-HP	60.24	30.91	This study
cMGK-HP	217.39	96.25	This study
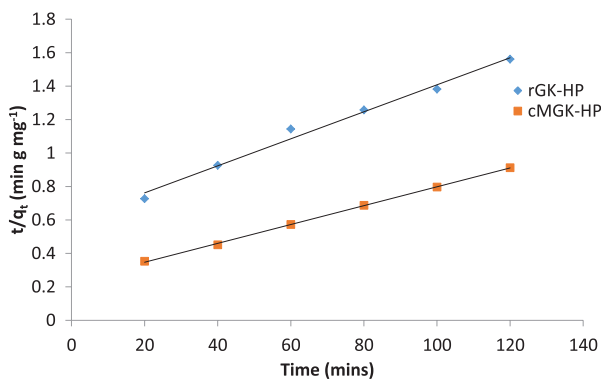
Figure 13. Pseudo second-order kinetic plots.

presented in Table 4. The presented R^2 values suggest Cr(VI) sequestration by rGK-HP and cMGK-HP to obey pseudo second order kinetic model ($R^2 > .99$). The significance of kinetic study is to understand the adsorption mechanism and also to optimize the adsorbent usage. This result suggests chemisorption is the rate-limiting step for the Cr(VI) ions adsorption onto the adsorbents.[68] Thus, a chemical reaction occurs between the adsorbents' surface and the Cr(VI) ions in solution.

$$In\left(q_e - q_t\right) = Inq_e - k_1 t \tag{5}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{6}$$

where q_e = equilibrium experimental adsorption capacity (mg g^{-1}), q_t = adsorption capacity at time t (mg g^{-1}), k_1 = pseudo first-order rate constant (min^{-1}) and k$_2$ = pseudo second-order rate constant (g mg^{-1} min^{-1}).

Thermodynamic study. Equations (7) and (8) were used to esti-mate change in standard Gibbs free energy (ΔG^o), standard enthalpy (ΔH^o) and standard entropy (ΔS^o) to know the ther-modynamics characteristics of Cr(VI) sequestration from solu-tion by rGK-HP and cMGK-HP. The thermodynamic parameters obtained via a plot of lnK_L versus $1/T$ (Figure 14) are presented in Table 5. The negative values of ΔH^o and ΔG^o suggest Cr(VI) sequestration to be spontaneous, feasible and exothermic in nature. The value of ΔG^o increased with increase in temperature which suggests adsorption feasibility at higher temperatures.[54] Nonetheless, the positive values of ΔS^o for both rGK-HP and cMGK-HP indicate high degree of disor-derliness at solid-liquid interface during Cr(VI) adsorption onto the adsorbents.[20]

$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{7}$$

$$InK_L = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \tag{8}$$

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.

Table 4. Kinetic parameters of Cr(VI) sequestration from aqueous solution by rGK-HP and cMGK-HP.

	$Q_{E(EXP)}$	PSEUDO-FIRST-ORDER			PSEUDO-SECOND-ORDER		
		$K_1 \times 10^{-2}$	$q_{e,(cal)}$	R^2	$K_2 \times 10^{-3}$	$q_{e,(cal)}$	R^2
rGK-HP	9.926	3.32	5.427	0.9023	2.24	9.745	0.9901
cMGK-HP	13.951	4.04	8.473	0.8941	1.96	13.454	0.9989
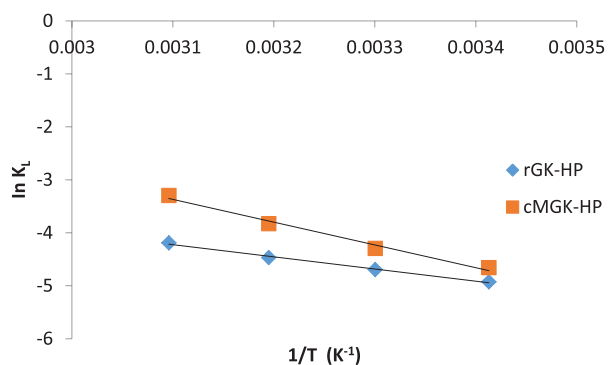
Figure 14. Plot of ln K_L versus 1/T (K^{-1}).

Regeneration and reusability of cMGK–HP

As shown in Figure 15, the Cr(VI) percentage removed decreased as the adsorption-desorption cycle number was increased. After the fifth regeneration of cMGK-HP, the Cr(VI)percentage removed from solution reduced from 96.29% to 91.05%. This could be linked to loss of some active sites on cMGK-HP surface in the process of dissolution. Also, the result revealed high potential of cMGK-HP to be used repeatedly for Cr(VI) sequestration from solution because the percentage removal was even greater than 90% after the fifth cycle. The cMGK-HP is robust and have high stability for sequestration of Cr(VI) from solution. The regeneration can continue without environmental contamination.

The spent adsorbent was incinerated between 650°C and 700°C in a muffle furnace for 7 hours to obtain ash. A solid-liquid ratio of 1:5 was obtained by dissolving 5 mg of the spent adsorbent in 25 mL of deionized water.[63] The mixture was filtered after stirring for 24 hours. Atomic absorption spectrophotometer was utilized to analyze the concentration of Cr(VI). Absence of Cr(VI) was noticed in the filtrate which strongly signifies the effectiveness of thermal treatment. The ash product can be used to soak up driveway spills, add traction to slippery walkways and keep harmful bugs away at home.
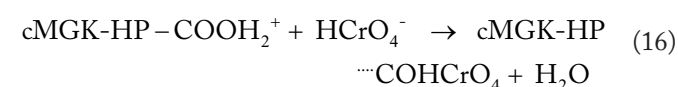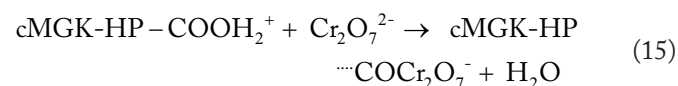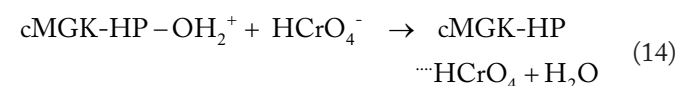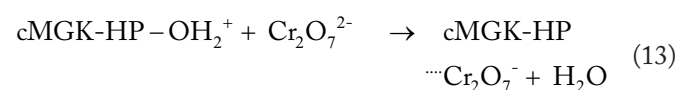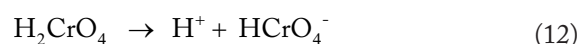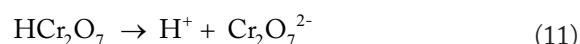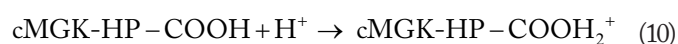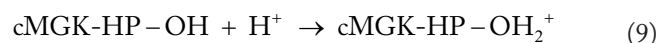
Adsorption mechanisms

The FTIR result earlier presented has shown the existence of strong -OH stretching vibration and bending of –COOH on cMGK-HP surface at 3332.2 and 1420.1 cm^{-1} wavelengths due to the alkaline hydrolysis of rGK-HP with NaOH.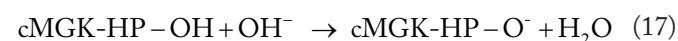 At a low pH, cMGK-HP surface is positively charged and becomes protonated as shown in equations (9) and (10). Also, oxy-anions (CrO$_4^{2-}$ and Cr$_2$O$_7^{2-}$) are formed in solution (equations (11) and (12)). Then, electrostatic attraction comes into play between Cr(VI) ions and oxygen-oriented functional groups (-OH and -COOH) on adsorbent surface as stated in equations (13)–(16). The increment in the amount of Cr(VI) adsorbed was enhanced by the attraction between H$^+$ ions and oxy-anions formed in solution. Also, the adsorbent matrix enhanced the adsorption by interacting with Cr(VI) ion through complexion and electrostatic interaction.[69] This also increases Cr(VI) volume removed from solution.

At high pH values, cMGK-HP surface becomes negatively charged as shown in equations (17) and (18). Also, HCrO$_4^-$ and CrO$_4^{2-}$ are formed in solution at this pH level as shown in equations (19) and (20). Thus, chromium compound oxy-anions compete together with the negative charge on cMGK-HP surface as presented in equations (21)–(24) to form complexes thereby reducing Cr(VI) amount sequestered.

At low pH:

$$cMGK\text{-}HP\text{–}OH + H^+ \rightarrow cMGK\text{-}HP\text{–}OH_2^+ \tag{9}$$

$$cMGK\text{-}HP\text{–}COOH + H^+ \rightarrow cMGK\text{-}HP\text{–}COOH_2^+ \tag{10}$$

$$HCr_2O_7 \rightarrow H^+ + Cr_2O_7^{2-} \tag{11}$$

$$H_2CrO_4 \rightarrow H^+ + HCrO_4^- \tag{12}$$

$$cMGK\text{-}HP\text{–}OH_2^+ + Cr_2O_7^{2-} \rightarrow cMGK\text{-}HP \cdots Cr_2O_7^- + H_2O \tag{13}$$

$$cMGK\text{-}HP\text{–}OH_2^+ + HCrO_4^- \rightarrow cMGK\text{-}HP \cdots HCrO_4 + H_2O \tag{14}$$

$$cMGK\text{-}HP\text{–}COOH_2^+ + Cr_2O_7^{2-} \rightarrow cMGK\text{-}HP \cdots COCr_2O_7^- + H_2O \tag{15}$$

$$cMGK\text{-}HP\text{–}COOH_2^+ + HCrO_4^- \rightarrow cMGK\text{-}HP \cdots COHCrO_4 + H_2O \tag{16}$$

At high pH:

$$cMGK\text{-}HP\text{–}OH + OH^- \rightarrow cMGK\text{-}HP\text{–}O^- + H_2O \tag{17}$$

Table 5. Thermodynamic parameters for Cr(VI) sequestration from solution by rGK-HP and cMGK-HP.

	ΔS^O (J/MOL K)	ΔH^O (KJ/MOL)	ΔG^O (KJ/MOL)			
			293 K	303 K	313 K	323 K
rGK-HP	+24.12	−19.11	−26.18	−26.42	−26.66	−26.90
cMGK-HP	+34.91	−27.66	−37.89	−38.24	−38.59	−38.94
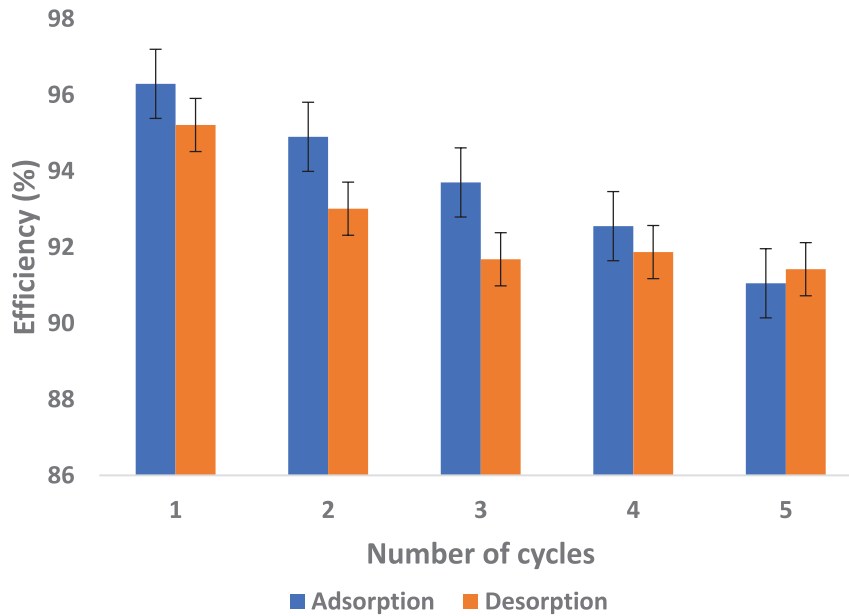
Figure 15. Cr(VI) Adsorption-desorption efficiency after 5 cycles using cMGK-HP.

$$cMGK\text{-}HP - COOH + OH^- \rightarrow cMGK\text{-}HP - COO^- + H_2O \quad (18)$$

$$Cr_2O_7^{2-} + OH^- \rightarrow HCrO_4^- + CrO_4^{2-} \quad (19)$$

$$HCrO_4^- + OH^- \rightarrow CrO_4^{2-} + H_2O \quad (20)$$

$$cMGK\text{-}HP - O^- + HCrO_4^- \rightarrow cMGK\text{-}HP - O^{\cdots}HCrO_4^{2-} \quad (21)$$

$$cMGK\text{-}HP - O^- + CrO_4^{2-} \rightarrow cMGK\text{-}HP - O^{\cdots}CrO_4^{3-} \quad (22)$$

$$cMGK\text{-}HP - COO^- + HCrO_4^- \rightarrow cMGK\text{-}HP - COO^{\cdots}HCrO_4^{2-} \quad (23)$$

$$cMGK\text{-}HP - COO^- + CrO_4^{2-} \rightarrow cMGK\text{-}HP - COO^{\cdots}CrO_4^{3-} \quad (24)$$
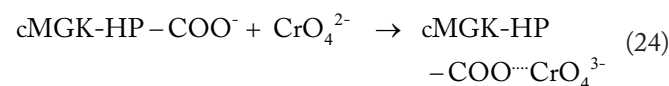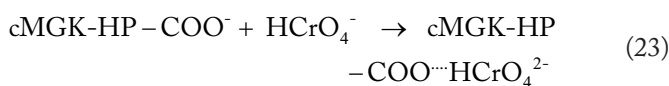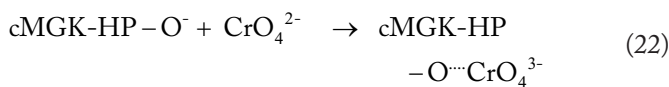
Impact of findings on environmental/public health

It is essential for researchers to contribute toward ways of reducing chromium contamination in our environment because of its carcinogenic and toxic nature. This study has shown the effectiveness of NaOH-hydrolyzed *Garcinia k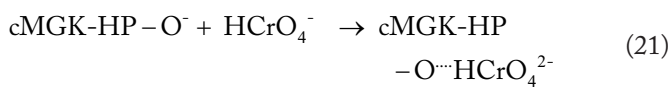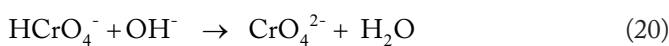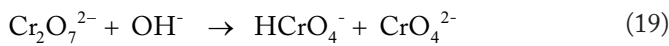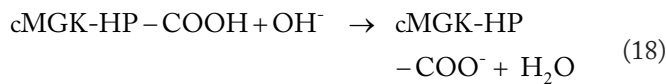ola* hull particles as an adsorbent to remove chromium ions from solution. Industries generating wastewater polluted with chromium can apply this low-cost adsorbent as a replacement to high-cost commercial activated carbon in their water treatment plants. The kinetic, isotherm and thermodynamics data generated are helpful in designing a pilot scale adsorption column which can be extended to large scale for chromium ions removal from solution. This study will also minimize the environmental pollution from *Garcinia kola* hull as they are useful in generating beneficial adsorbent to remove chromium ions for public use.

Conclusions

This study has examined a comparative analyses between using rGK-HP and cMGK-HP for Cr(VI) sequestration from solution. Chemically-modified GK-HP proved effective for Cr(VI) sequestration than rGK-HP. It possesses excellent thermal stability, textural and reusability attributes. It can remove 96.25% of Cr(VI) from solution at a pH of 2, a temperature of 40°C, an adsorbent dosage of 8 g/L, a contact time of 60 minutes and Cr(VI) initial concentration of 20 mg/L. The Cr(VI) percentage removed from solution decreased with increasing pH and adsorbate initial concentration but increased with increasing contact time, adsorbent dose and temperature. SEM, BET, FTIR, XRD and EDS revealed change in

morphological structure, textural property, spectral peak, phase composition and chemical composition of rGK-HP and cMGK-HP before and after Cr(VI) sequestration. The pH_{pzc} reduced from 6.29 to 2.41 when rGK-HP was modified to cMGK-HP with NaOH. Adsorption data fitted with Langmuir isotherm and pseudo second order kinetic models. Adsorption was spontaneous, feasible and exothermic in nature. In conclusion, cMGK-HP could be effectively used for Cr(VI) removal.

Acknowledgements

Author Contribution

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.

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