*Research Article*

# Enhanced Adsorptive Removal of Chromium (VI) from Aqueous Solution on Using Aged Refuse: Resource Recovery and Environmental Applications

**B. Manimekalai [iD],[1] S. Sivanesan [iD],[2] and P. Senthil Kumar [iD][3,4,5]**

[1]*Centre for Environmental Studies, Anna University, Chennai, 600025 Tamil Nadu, India*
[2]*Department of Applied Science and Technology, AC Tech Campus, Anna University, Chennai, 600025 Tamil Nadu, India*
[3]*Department of Chemical Engineering, Sri Sivasubramaniya Nadar College of Engineering, Chennai, 603110 Tamil Nadu, India*
[4]*Centre of Excellence in Water Research (CEWAR), Sri Sivasubramaniya Nadar College of Engineering, Chennai, 603110 Tamil Nadu, India*
[5]*School of Engineering, Lebanese American University, Byblos, Lebanon*

Correspondence should be addressed to S. Sivanesan; siva@annauniv.edu and P. Senthil Kumar; senthilkumarp@ssn.edu.in

"Aged refuse" corresponds to municipal solid waste material dumped in land, for several years. This solid waste material is chosen as an adsorbent for the current study since it is available abundantly in the state of Tamil Nadu, India, and has not been used for any other applications. The current study was conducted to get rid of the element chromium (VI) from wastewater by using the adsorption process. The aged refuse was analytically tested through various processes such as BET, TGA, XRD, SEM, and FTIR to determine the surface morphology, functional groups, thermal stability, nature of the crystalline, and surface area. The researchers conducted the batch adsorption study to validate the influence exerted by different sorts of adsorption parameters like contact time (10-100 min), initial concentration of the pollutant (50 mg·L$^{-1}$ to 250 mg·L$^{-1}$), pH (1-7), and the dosage of the adsorbent (0.5 g·L$^{-1}$-3.0 g·L$^{-1}$). In the current study, the researchers achieved the maximum adsorption capacity of 195.54 mg·g$^{-1}$. From the kinetic results, it can be understood that the pseudo-first-order model was the most suitable kinetic model. Further, the study outcomes confirm that the Langmuir isotherm model is the best fit by isotherm studies which indicate the monolayer adsorption process. This study indicated that the aged refuse can be potentially used in removing Cr (VI) from water environment under standard optimized conditions.

## 1. Introduction

Across the globe, certain types of industries like electroplating, petrochemicals, and chemical synthesis release heavy metals as pollutants in water resources. Among these, the electroplating industries release a significant volume of heavy metals through wastewater. These heavy metals include platinum, chromium, zinc, silver, lead, cadmium, titanium, nickel, vanadium, and copper. In addition to this, some other industries, such as tanneries, pigment and dyeing units, petroleum refining industries, leather, textile, wood processing, paint, and photographic film manufacturers, discharge huge volumes of heavy metals and pollute the environment. Such heavy metals remain toxic not only to human beings, but the animals also. It threatens the existence of life forms on earth, especially the aquatic environment, and gets biomagnified across the hierarchies of the food chain [1].

Chromium is present in trivalent and hexavalent forms in the aqueous solution [2, 3]. The World Health Organization allowed certain permissible limit for the element, i.e., 0.1 mg·L$^{-1}$ in the case of surface water, whereas in the case of drinking water, it should be 0.05 mg·L$^{-1}$ [4]. Excessive load of chromium may lead to immunological disorders, liver and

larynx irritation crevice, nasal septum, asthma, and bronchitis. Contact of chromium with the skin may lead to skin irritation, sensitivities, and dermatitis. They have the capacity to tie the twofold stranded deoxyribonucleic acid that alters the gene replication and alterations [5]. To mitigate the amount of chromium in wastewater, several treatment methods have been proposed and validated in literature such as the chemical precipitation, coagulation, electrocoagulation, solvent extraction, and ion exchange [6, 7]. However, these methods are found to be less effective in getting rid of the element. In comparison with the rest of the processes, the adsorption process is cost-effective and simple to execute [8, 9]. Different types of biosorbents are used in general such as sugarcane bagasse, vineyard pruning, and orange peel for the removal of chromium ions. One of the main specialties of these biosorbents is that it contains numerous functional groups like amino, carboxyl, hydroxyl, and phosphate on the cell wall which assist in the eradication of toxic pollutants from water [10]. These two entities disintegrate very slowly since the dyes are exceedingly complex whereas the metals cannot be degraded. So, different treatment processes are required to treat the effluents discharged by multiple types of sectors such as the dyeing industry, textile units and tanneries, metal plating, alloy industries, mining and smelting processing units, chloralkali, and radiator manufacturing units. Some of the commonly applied methods to reduce the quantity of heavy metal ions and dyes in the released effluents include ion exchange, lime precipitation, membrane processing, adsorption onto activated carbon, and electrolysis [11].

Having been identified as a mass transfer process, the migration of an element occurs from the liquid phase to the surface of a solid during the adsorption process. Some of the liquid phase components in this process get interchanged with the outer layer of the solid adsorbents. The adsorption process is executed through three modes in general such as the semibatch, batch, and continuous modes. Adsorption generally occurs because of the attractive interfaces that exist between a surface and the absorbed group at the molecular level. When compared with the traditional heavy metal removal processes, the adsorption process is highly advantageous in terms of cost-effectiveness, regenerative capacity, metal selectivity, recovery of the metal, efficiency, and nongeneration of toxic sludge. Various cost-effective adsorbents have been validated earlier based on natural and anthropogenic sources to be used in the treatment of wastewater with heavy metals. The studies conducted earlier leveraged cost-effective adsorbents such as industrial byproducts, agricultural waste, natural materials, or modified biopolymers [1].

Aged refuse refers to the waste material dumped in landfills for more than a decade and becomes stabilized and aged [12]. Aged refuse remains an unused resource that gets accumulated in the landfill and is difficult to manage [13]. Some of the aged refuse's properties are inclusive of volumetric weight, porosity, high organic content, and good adsorption capability. It can be used in wastewater treatment processes since it is a type of biological medium containing vast amounts of bacterial population (Qingmei [14]). Further, it has a large specific area, heavy moisture retention capacity, and high porosity. It also provides pH buffering capability.

Waste materials like low-cost adsorbent are more interesting to study than the rest of the adsorbents since it contributes to cost reduction through waste disposal. The guidelines framed by the World Health Organization (WHO) confine the concentration of chromium within the threshold, which leads to serious health consequences to mankind. According to the researchers [15], the research interest towards landfill is increasing nowadays since the materials excavated from the landfill can be recycled. Many researchers highlighted that the stabilized solid waste from bioreactor landfill operation can be used for the treatment of wastewater. Further, the researchers also focused on understanding the characteristics of surface area in aged refuse for wastewater treatment. The composition of the aged refuse is inclusive of 4.53% organic content with a particle size of 0.2 to 1 mm, while the organic content sized below 0.2 mm is 5.69% [13]. To better understand the significance of these naturally occurring complex minerals, the characteristics of the hematite loaded on kaolin clay complexes were examined earlier (Shuai [16]). Various authors proposed to make a fair use of adsorbents to get rid of most of the metals in water. Islamuddin et al. [17] opined that the adsorbents, which are easily available to conduct the adsorption investigations, are nothing but the elements from other areas such as horticulture and nourishment entities.

The current research work is aimed at getting rid of the metal, i.e., chromium (VI) ions, from the aqueous solution on aged refuse as the adsorbent. One of the main parts of this research is aged refuse used as raw material in the production of adsorbent. This highlights the reuse of waste into some useful carbon that has application in the water/wastewater treatment. The experiment was conducted in batch mode. The adsorbent was characterized by several analytical techniques to understand its physical and chemical characteristics. Adsorption isotherms and kinetic models were also studied for the removal of toxic chromium ions from water environment.

## 2. Experimental Methods

*2.1. Preparation of the Adsorbent.* The dumped solid waste was collected from the Pallikaranai dumping yard, Chennai, India. Solid materials sized less than 20 mm were considered for the study. The collected solid waste materials were sieved and sun-dried. Then, the material was activated by immersing in sulphuric acid for 24 h. Afterwards, the sample was filtered and incubated in an oven for the purpose of drying up to $100^\circ$C for about 24 h. The dried sample was then taken from the oven and allowed to cool at normal room temperature (RT). Afterwards, mortar was used to crush the solid particles. The resultant fine powder was used as the adsorbent for the study.

*2.2. Preparation of the Aqueous Solution.* In this study, the researchers made use of potassium dichromate ($K_2Cr_2O_7$) for chromium source whereas the stock solution was prepared by mixing an adequate amount of potassium dichromate in 1,000 mL of distilled water. From this stock solution, different concentrations of the working standard

solutions were made-up using the distilled water and the stock solution to conduct the adsorption study.

*2.3. Characterization of Aged Refuse Adsorbent.* The researchers used scanning electron microscope (SEM) (JSM–7100F) to study the surface morphology of the adsorbent. Prior to the investigation, the sample was gold sputtered. Energy dispersive X-ray spectroscopy was utilized to identify the sample's chemical composition. Further, the researchers conducted the Fourier transform infrared (FTIR) spectroscopy to evaluate the existence of functional groups on the sample surface. The researchers executed the BET (Brunauer-Emmett-Teller) analysis to study the porosity of the material and its surface area. In addition to these, the crystalline/amorphous nature of the sample was determined by following the powdered X-ray diffraction (XRD) technique. With the help of thermogravimetric analyzer–differential scanning calorimeter, the researchers measured the thermal stability of the sample. PSA was used to ensure the size of the aged refuse particles. CHNS analyzer was utilized to perform ultimate analysis upon the aged refuse.

*2.4. Experimental Procedure.* The researchers conducted the experiments in 250 mL flasks with an electric shaker in an ambient temperature. Various parameters were investigated to determine the impact of adsorption factors like the dosage of the adsorbent (0.5-3 g/L), pH (2-7), initial concentration of pollutant (50-250 mg·$L^{-1}$), and contact time (10-90 min) on 100 mL of aqueous solution. The samples were kept in an orbital shaker for the required contact time after which it was filtered using a Whatman filter paper. Atomic absorption spectroscopy (AAS) was used to determine the chromium (VI) ion concentration in the aqueous solution. The parameters of the batch adsorption studies were observed, and the optimum pH, contact time, and dosage were identified for the pollutant concentrations. In the case of heavy metals, AAS technique is utilized to determine the initial and final concentrations of the aqueous solution. Equation (1) is used to determine the equilibrium adsorption capacity of the aged refuse.

$$Q_e = \left( \frac{(C_o - C_e)}{m} \right) * V. \tag{1}$$

Here, the equilibrium adsorption capacity is denoted by $Q_e$ for the adsorbent (mg/g), and the pollutant's concentration at the initial time of the experiment is denoted by $C_o$, whereas $C_e$ corresponds to the pollutant's equilibrium concentration (mg·$L^{-1}$), the adsorbent's experimental (g) mass is portrayed by $m$, and finally, the volume of chromium solution (L) is given as $V$.

## 3. Results and Discussions

### 3.1. Characterization of Aged Refuse

*3.1.1. BET Analysis.* In the current study, the authors followed the BET method to find out the sample's exclusive surface area in line with the nitrogen adsorption isotherm measurements at 77 K. The BET method is useful to identify
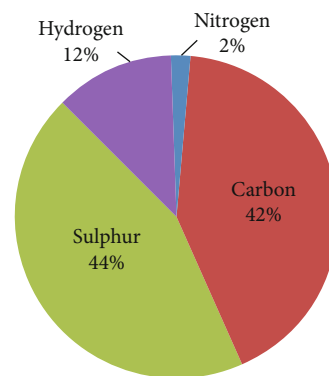


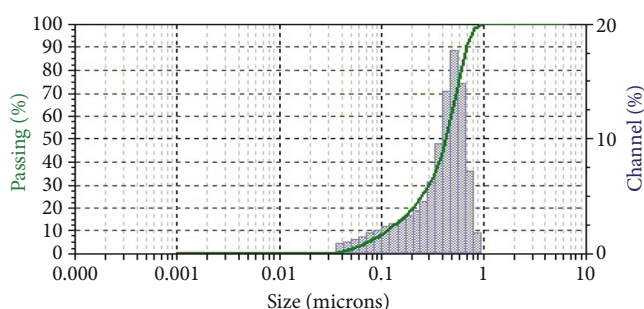Figure 1: Ultimate analysis outcomes of the aged refuse.



Figure 2: Particle size analysis.

the textural properties of the adsorbent. The raw aged refuse had a BET surface area of 286.717 $m^2$/g without treating it with Cr (VI).

*3.1.2. Ultimate Study of the Aged Refuse.* CHNS instrument was used to conduct the elemental analysis to determine the percentage compositions of carbon, nitrogen, sulphur, and hydrogen samples of the aged refuse. The ultimate analysis of the aged refuse was characterized, and Figure 1 shows the carbon, sulphur, nitrogen, and hydrogen contents present in the aged refuse. The presence of sulphur might be either due to the treatment of aged refuse with sulphuric acid or from the existing municipal solid waste dump yard which is a huge source of waste.

*3.1.3. Particle Size Analysis.* In general, an adsorbent material's particle size tends to create an impact on its characteristics, performance, and quality. So, it is essential to validate the stability of the material in suspension, its appearance, viscosity, reactivity, packing density, flow, texture, flavor, and other such characteristics. The performance of a material is easily assessed in line with its particle size [18]. Figure 2 shows the size of the adsorbent particles that lie in the range of 0.1 to 1 micron.

*3.1.4. SEM/EDAX Analysis.* The existence of heavy metals in the adsorbent, prior to the adsorption process, may obstruct the adsorption process. It may also lead to the formation of oxides in the presence of oxygen. Henceforth, the spectrum should be taken prior to the adsorption process [13]. Figures 3(A) and 3(B) show the SEM analysis of the
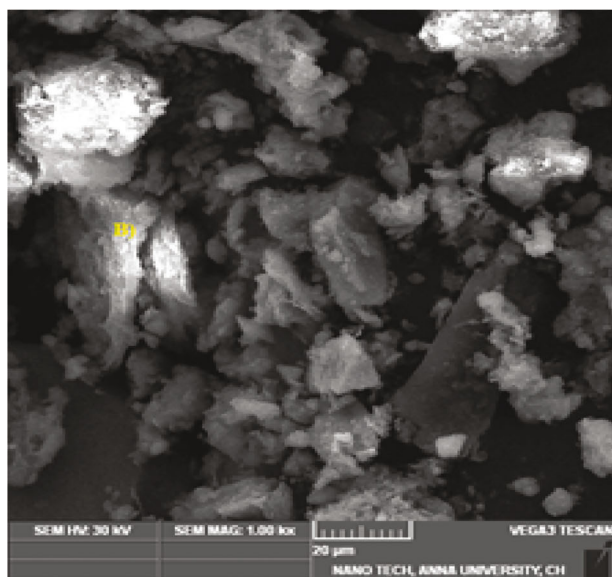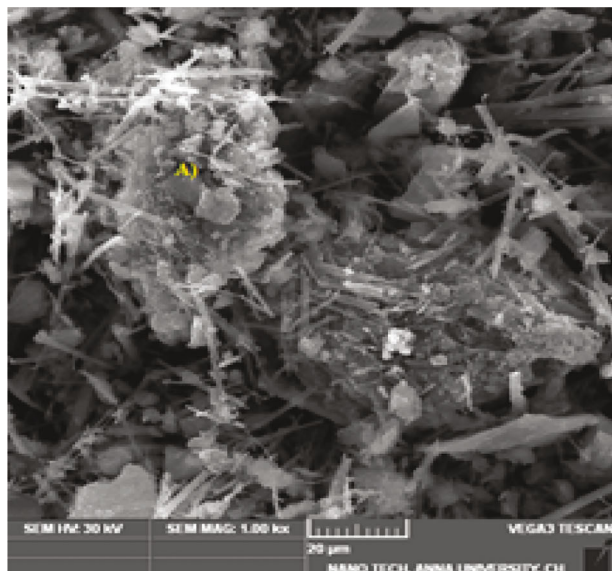
Figure 3: (A) SEM analysis of the chemically treated aged refuse. (B) SEM analysis of the raw aged refuse.

chemically treated aged refuse (adsorbent) and the raw material, respectively, which is utilized to validate the structural characteristics of the surface. The surface of the aged refuse was found to be smooth with a uniform microporous structure like rock and needle-like structures. The particles were quite large in line with the particle size analysis outcomes. Figure 4 displays the elements present in the aged refuse, i.e., silica content was around 45.54% and oxygen was 50.23%, whereas the rest of the elements were negligible.

*3.1.5. FTIR Analysis.* FTIR is a crucial analytical technique that is used in the investigation of functional groups on a solid surface. These functional groups are nothing, but the structural units of the organic compounds are defined by specific atom and bond arrangements. Figures 5 and 6 show the FTIR curves of the aged refuse adsorbent and the raw material of the aged refuse. IR was conducted for both the
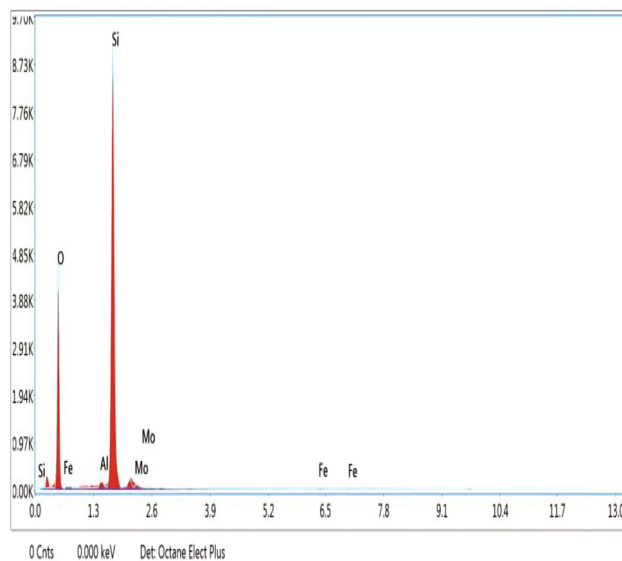


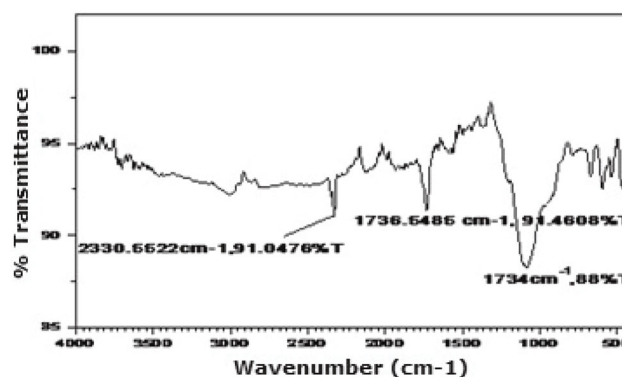Figure 4: EDAX analysis results of the aged refuse.



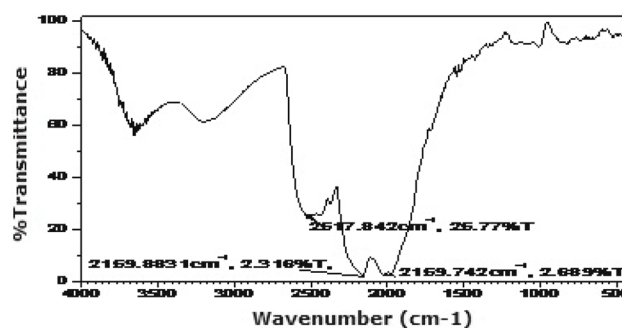Figure 5: FTIR analysis of the chemically treated aged refuse.



Figure 6: FTIR analysis of the raw material.

samples, i.e., raw and posttreatment with sulphuric acid. As mentioned earlier, Figures 5 and 6 show the FTIR spectra of the aged refuse adsorbent after acid modification and as raw material, respectively. The figure shows the peaks at $1039.5\ cm^{-1}$ because of C–O and C–H bonds, respectively. In general, some of the crucial sorption sites include carboxylic (COOH), phenol (OH), amine (NH), and carbonyl (C=O) groups. In the biosorbent, the existence of carboxylic
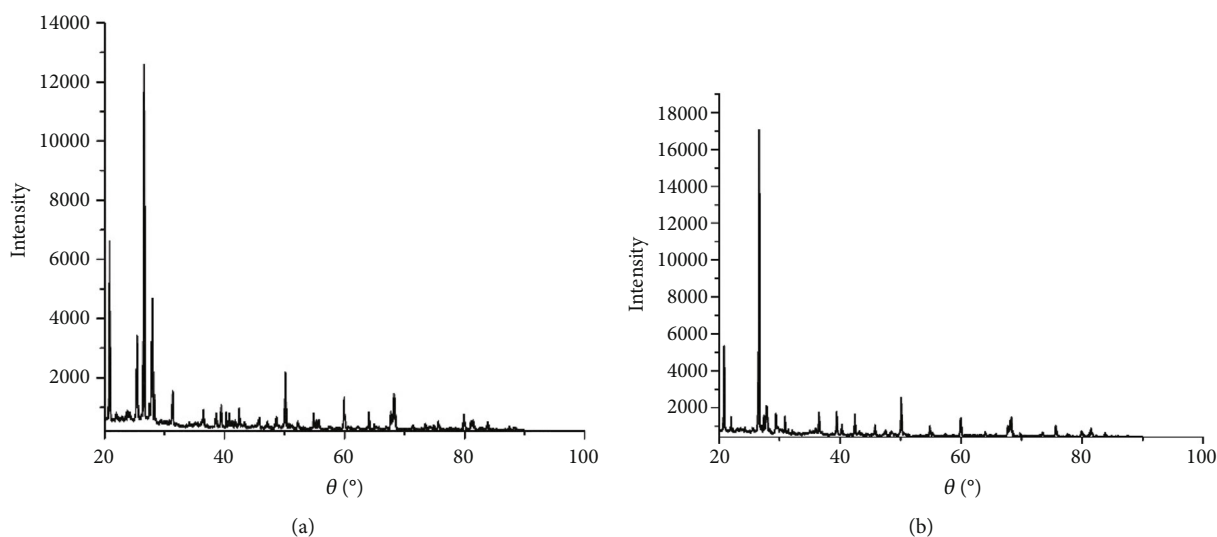
Figure 7: (a) XRD of the chemically treated aged refuse. (b) XRD of the raw aged refuse.

acid groups can be confirmed through the presence of –OH group in association with carbonyl group [19]. Such wavelength migrations infer the occurrence of metal binding process at the absorbent. In general, hydroxyl groups are an important functional group that plays a role in the adsorption process. Further, the unsaturated groups such as the carboxylate anion C=O and alkene are also accountable for chromium adsorption like the previously mentioned adsorbents. This phenomenon can be understood from the shift of the peak more than 10 cm⁻¹. FTIR peaks were found around $2330.5522 \, cm^{-1}$ in the aged refuse sample after activation. This phenomenon corresponds to the triple bond region and amino-related compounds. Another peak was found at $1736.5485 \, cm^{-1}$ which corresponds to double bond regions such as C=C, C=O, and C=N associated with the carbonyl compound, i.e., a six-membered ring lactone. It corresponds to the common carbonyl compounds such as the esters or carboxyl, ketones, and aldehydes that lie in the range of 1750 and $1700 \, cm^{-1}$, and this occurs because of the bonding between the benzene ring and methyl (CH$_3$) [20]. The peak was found around $2517.84 \, cm^{-1}$ in the aged refuse raw material sample without acid activation due to the presence of thiols (S-H stretch).

*3.1.6. XRD Analysis.* The peak values were attained around 20° and 30° while the sample was crystalline in nature due to the increased intensity at 28°C. The displacement of the high intensity peaked at 28° (raw material) and 27° (adsorbent). This displays the characteristic change in the acid-treated material. Figures 7(a) and 7(b) show that the peak values can be identified for various intensities and the corresponding theta value.

*3.1.7. TGA Analysis.* Figures 8(a) and 8(b) show the scale of the graph from 0 to 800°C. There was 20% degradation in the untreated material (raw aged refuse) whereas the chemically activated adsorbent material recorded an 8% degradation percentage. The adsorbent material was chemically stable until 800°C. From the graph, the adsorbent

(chemically treated aged refuse) was found to be thermally highly stable compared to the raw material. With an increase in temperature from 200°C to 400°C, the stability also increased heavily. After a certain temperature, the stability remained constant.

*3.2. Adsorption of Chromium (VI) Ions*

*3.2.1. Effect of Adsorbent Dosage.* Figure 9 shows various dosages of the absorbent from which it can be inferred that the chromium (VI) got removed to the highest possible extent at $1.5 \, g \cdot L^{-1}$ dosage than the lower dosages of the absorbent. The researchers prepared varying concentrations of the aged refuse in 100 mL of the aqueous solution investigated at pH 3 and at 30°C. When the adsorbent's dosage increased, there was a proportionate increase in the removal of Cr (VI) too. This is attributed to the availability of excess count of the binding sites because of the huge surface area of the absorbent. But the increasing dosage of the adsorbent showed no impact on the removal of chromium once equilibrium was reached. This might be due to the unavailability of the Cr (VI) ions in the solution to make use of the binding sites upon the aged refuse adsorbent [21, 22]. With the availability of huge number of adsorption sites with large surface area of the absorbent, there was a high removal of chromium ions observed at high dosage of the adsorbent [19, 23]. After reaching the equilibrium, there were no sufficient chromium ions to leverage the active sites due to which the adsorption reached a constant value [24]. In the case of incrementing the dosage of the adsorbent, it automatically enhanced the count of active sites present for the purpose of adsorption. So, this phenomenon, i.e., enhancing the ion/proton exchange between the functional groups and the active sites, is a valuable technique to enhance the overall adsorption rate (Aiping [25]).

*3.2.2. Effect of pH.* A solution's pH value is crucial since it keeps the adsorption of metal ions under control. However,
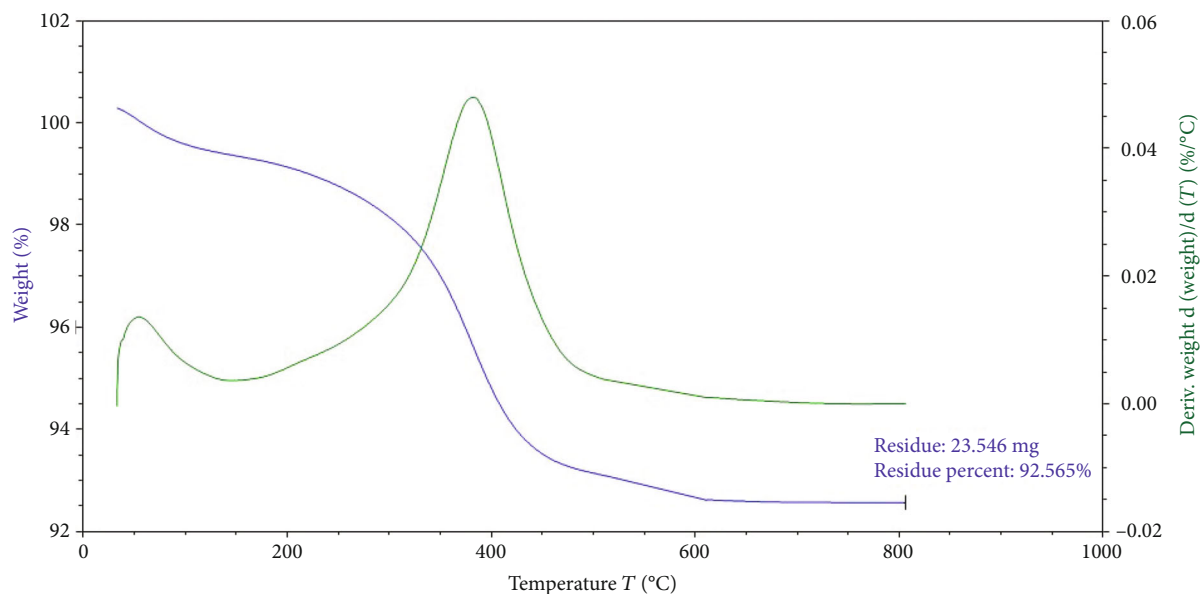
(a)
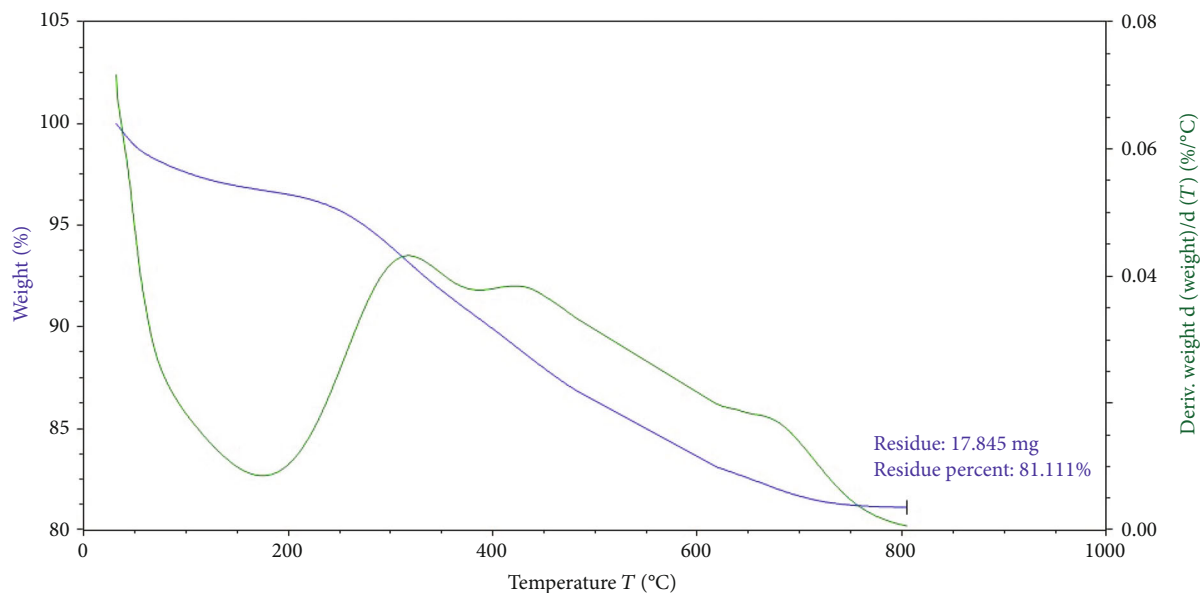


(b)

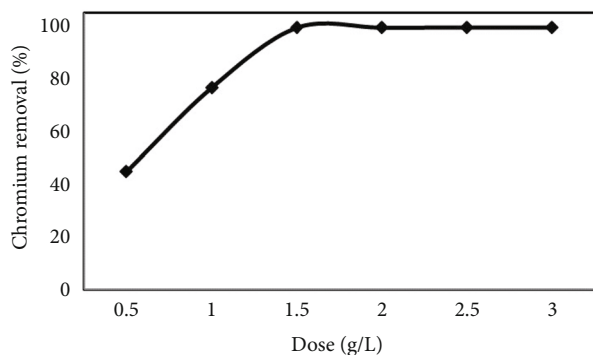Figure 8: (a) TGA of the chemically treated aged refuse. (b) TGA of the aged refuse.



Figure 9: Influence of adsorbent dose on chromium (VI) removal.

the functional groups present in an adsorbent only decide the pH value. Corresponding to the solution chemistry, the high presence of $H^+$ ions on the adsorbent's surface denotes a low pH. A significant and a strong electrostatic attraction got produced due to the presence of $HCrO^{-4}$. In the event of enhancing the pH value from 1 to 10, there was an increase observed in chromium efficiency too up to pH 3. But it diminished when the pH value reached 7. Below pH 3, the surface-bound functional groups carry positive changes. Once it moves to the higher end, the surface of the adsorbent contains a high count of negatively charged functional groups. According to the literature, the repulsion was enhanced between the adsorbent and the Cr (VI) ions
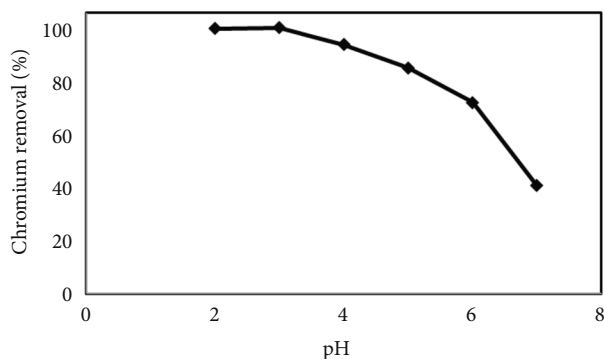
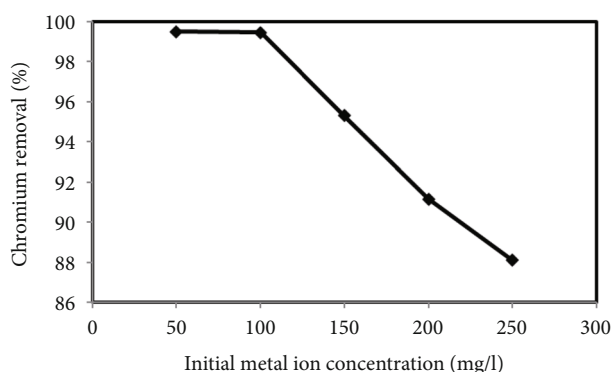FIGURE 10: Effect of aqueous solution pH on chromium (VI) removal.



FIGURE 11: Initial metal ion concentration impact on chromium (VI) removal.

[26]. The solutions' pH creates an impact of the surface properties of the adsorbent and the Cr ions' active form [21].

In this study, 1.5 g of aged refuse adsorbent was mixed with 100 mL of aqueous solution and stirred for 60 min at 30°C while the initial ion concentration was maintained at $100 \, mg \cdot L^{-1}$. Figure 10 shows the chromium removal for different pH ranges. The figure infers that pH 3 portrayed the maximum possible elimination of Cr (VI) ions. With a gradual increment in the pH from 2 to 7, there was a strong decline in the Cr (VI) removal efficiency from 99% to 40%. This shows that the removal of chromium at acidic condition was high. Before pH 3, the hexavalent chromium was in deprotonated form whereas it reached a protonated form above pH 3 due to which it got easily dissolved in the aqueous solution. In general, $HCrO_4^-$, in its precipitated form, chromium ions are not toxic whereas once it gets dissolved in the water, it becomes carcinogenic. The highest possible Cr (VI) ion removal was attained at 25°C and pH 5 within 90 min using eggshell as an adsorbent [27].

*3.2.3. Effect of Initial Chromium (VI) Ion Concentration.* Figure 11 shows the influence exerted by the initial metal ion concentration on the Cr (VI) removal. The batch study was conducted at different initial ion concentrations in the range of $50 \, mg \cdot L^{-1}$ to $250 \, mg \cdot L^{-1}$. The study parameters were as follows: time period, 60 minutes; optimum pH, 3; adsorbent dosage level, $1.5 \, g \cdot L^{-1}$ mixed in 100 mL of aqueous
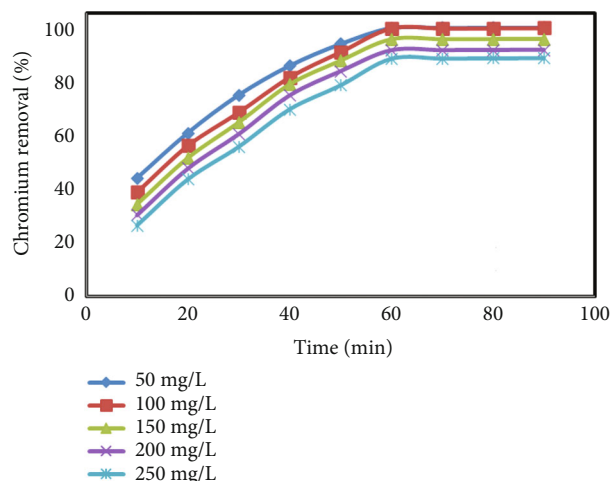


FIGURE 12: Impact of contact time on chromium (VI) removal.
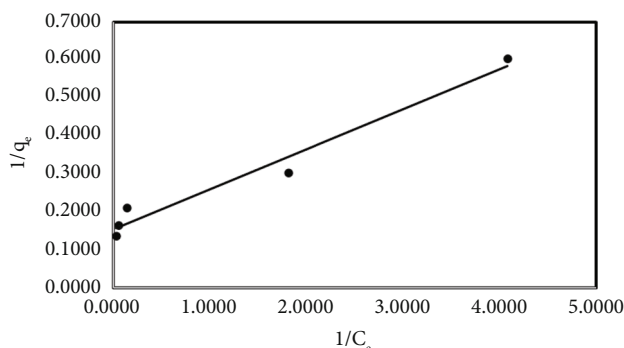


FIGURE 13: Langmuir isotherm model fit for chromium (VI) removal.
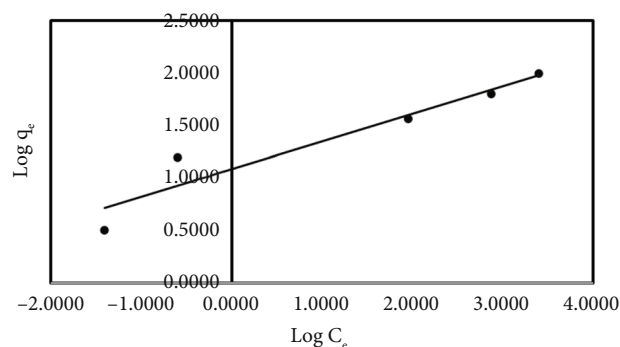


FIGURE 14: Freundlich isotherm model fit for chromium (VI) removal.

solution at various metal ion concentrations; and temperature, 30°C. The results infer that the removal percentage was maximum at $100 \, mg \cdot L^{-1}$ concentration while it got gradually reduced at high concentration of the initial metal ion.

Initial ion concentration remains a crucial factor since it triggers to overperform the mass transfer resistance exhibited by the metal ions between the adsorbent and the aqueous solution [28]. This can be detailed with the help of high contact between the adsorbate and the adsorbent surface's activated sites. Rai et al. [24] hypothesized that

TABLE 1: The Langmuir and Freundlich isotherm constants.

| | Langmuir | | | Freundlich | | |
|---|---|---|---|---|---|---|
| $Q_{max}$ (mg/g) | $K_L$ (L/mg) | $R^2$ | $K_F$ $((mg/g)(L/mg)^{1/n})$ | $n$ | $R^2$ |
| 195.54 | 1.461 | 0.9692 | 88.85 | 3.795 | 0.9132 |

the available sites remain occupied and saturated after threshold from the initial Cr (VI) concentration. According to Sudha and Emilia Abraham [29], a low ratio exists between the number of available activated sites and the Cr (VI) ions, when the concentration of Cr (VI) is high. As a result, a decline can be observed in the Cr (VI) removal efficiency, when the concentration of the adsorbent was high. Further, a decline in the removal efficiency of chromium (VI) can be observed at high concentrations due to the saturation of the adsorption sites. However, when the concentration is low, the possibilities are high for the interaction between the metal ions and the adsorption sites. This generally enhances the removal efficiency. A better concentration gradient can be achieved by high concentration of the metal ion which remains a crucial factor to conquer the mass transfer resistance of metal ion between the liquid and solid phases [19]. The rationale behind the presence of large concentration gradient between the sorbent phase and bulk solution remains the uptake at higher initial concentration [30].

*3.2.4. Effect of Contact Time.* The impact of the contact time on chromium removal efficiency is shown in Figure 12. The optimum parameters for this investigation were as follows: pH 3; temperature, 30°C; and adsorbent dosage, 1.5 g·L$^{-1}$, and volume of the aqueous solution was 100 mL for an initial metal ion concentration of 100 mg·L$^{-1}$. The metal ions got adsorbed rapidly in the initial stage because of the huge initial concentration gradient that exists between the count of available vacant sites on adsorbent's surface and the adsorbate that exits in the solution [19]. The maximum number of active sites is available at the initial stages of adsorption for the maximum removal of pollutant from the aqueous solution [31]. At first, most of the active sites present on the adsorbent remained unoccupied due to which the adsorption occurred rapidly. On the other hand, desorption process got initiated at a low rate. The overall adsorption effect rapidly increased. After the occupation of the active sites, equal adsorption and desorption rates were observed. This can be interpreted as a reduction in the adsorption rate which became constant at equilibrium [24]. The maximum chromium (VI) ion removal was obtained at 60 min.

## 3.3. Adsorption Isotherm Studies

*3.3.1. Langmuir Isotherm Model.* In this study, the Langmuir and Freundlich models are used to analyze the removal of Cr (VI) from the aqueous solution using the aged refuse at an equilibrium condition. In general, the Langmuir isotherm model is useful to investigate the monolayer adsorption upon the adsorbent's exterior side that contains limited number of equivalent and identical sites. On the other hand,



FIGURE 15: Pseudo-first-order model fit for chromium (VI) removal.
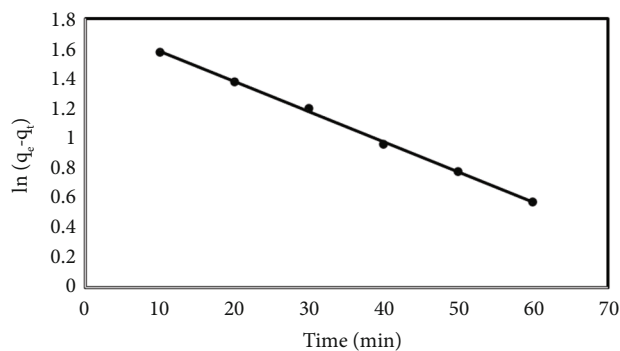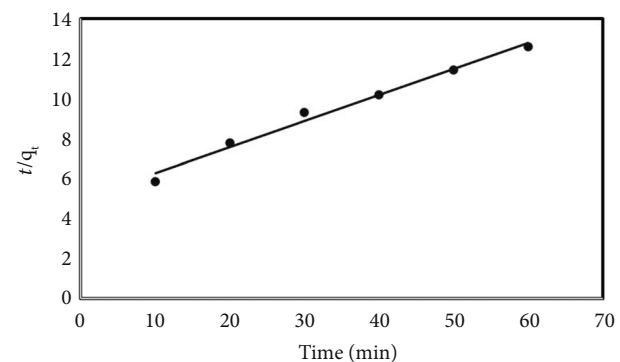


FIGURE 16: Pseudo-second-order model fit for chromium (VI) removal.

the Freundlich isotherm model is usually implemented in case of multilayer adsorption. Equation (2) shows the general representation of the Langmuir isotherm model.

$$\frac{1}{q_e} = \frac{1}{q_m K_L C_e} + \frac{1}{q_m},\qquad(2)$$

where the highest possible adsorption capacity is denoted by $q_m$ (mg·g$^{-1}$) to generate a whole monolayer coverage on the outer layer at high equilibrium adsorbate concentration ($C_e$) (mg·L$^{-1}$) and $K_L$ (L/mg) corresponds to the Langmuir constant which is related to the affinity between the adsorbent and the adsorbate [32]. Figure 13 shows the Langmuir isotherm for chromium (VI) removal which depicts the $R^2$ value. In this method, the Langmuir constants such as $q_m$ and $K_L$ are found with the help of slope and intercept values in the plot between $1/q_e$ and $1/C_e$, respectively.

*3.3.2. Freundlich Adsorption Isotherm.* Being an empirical model, the Freundlich isotherm model is created in line with

TABLE 2: Kinetic model parameters for chromium removal.

| Pseudo-first-order | | | | Pseudo-second-order | | | |
|---|---|---|---|---|---|---|---|
| $k_1$ (min$^{-1}$) | $q_{e,cal}$ (mg/g) | $q_{e,exp}$ (mg/g) | $R^2$ | $k_2$ (mg$^{-1}$·min$^{-1}$) | $q_{e,cal}$ (mg/g) | $q_{e,exp}$ (mg/g) | $R^2$ |
| 0.0272 | 177.94 | 195.54 | 0.9989 | 0.0019 | 232.56 | 195.54 | 0.9852 |

TABLE 3: Comparison of chromium removal from aqueous solution using aged refuse with other adsorbents.

| Type of the adsorbent | Mode of the study | Optimum values in operating conditions | Kinetic studies/ modeling | Adsorption capacity/ %removal | Reference |
|---|---|---|---|---|---|
| Chemically modified dried water hyacinth roots | Batch | pH=3; adsorbent dose = 14 g/L; adsorbent conc. = 10 mg/L; temp = 25 ± 5°C; contact time = 2 hr | Freundlich isotherm; pseudo-second-order; Weber-Morris intraparticle diffusion | 95.43% | [36] |
| Unmodified saw dust | Batch and column study | pH = 8.29; contact time = first 2 min; temp = 25 to 60°C | Freundlich model; pseudo-second-order | 99% at first 2 minutes | [37] |
| Magnetic snail shell | Batch study | pH=3; contact time = 150 min; initial conc. = 60 mg/maximum; adsorbent dose = 20 mg/25 min | Pseudo-second-order; Langmuir isotherm | 18.89 mg/g | [38] |
| Palm oil fuel ash (POFA) | Batch adsorption study; column adsorption study | pH = 2; adsorbent dosage = 80 g/L; contact time = 6 min | Freundlich isotherm; pseudo-second-order | 0.464 mg/g | [21] |
| Low-cost adsorbents (groundnut seed cake powder, sesame seed cake powder, coconut cake powder) | Batch adsorption technique | pH = 2; contact time = 1 hr (60 min); dosage = 0.6 g; initial ion concentration = 50 mg/L; temperature = 40°C | Langmuir isotherm; pseudo-second-order | 99.7% removal | [26] |
| Groundnut shell | Batch experiments | Contact time = 120 min; pH = 8; adsorbent dose = 2 g/L; initial metal ion concentration = 25 mg/L; temp = 41.5°C | Temkin isotherm | 96 mg/g | [19] |
| Graphene oxide (GO) prepared from graphite | Batch mode | pH = 4; adsorbent dosage = 0.01 g; contact time = 40 min; temp = 70°C | Langmuir model | 92.8% acidic pH = 4 | [31] |
| Amine impregnated crab shells | Batch process | Temperature = 15°C; initial concentration of Cr (VI): 100 mg/L; adsorbent concentration: 1.0 g/L; initial solution pH: 2.0 | Langmuir model; pseudo-second-order | 36.865 mg/g | [39] |
| Sulphuric acid modified aged refuse | Batch study | pH = 3; adsorbent dosage = 1.5 g/L; contact time = 60 min; temperature = 30°C; initial chromium (VI) ions concentration = 50 – 250 mg/L | Langmuir and pseudo-first-order | 195.54 mg/g | Present study |

the adsorption in a heterogeneous surface. The linear form of the Freundlich isotherm model is portrayed as

$$\ln (q_e) = \ln (K_F) + \left(\frac{1}{n}\right) \ln C_e \qquad (3)$$

Here, $K_F$ denotes the Freundlich constant ((mg/g) (L/mg)$^{1/n}$), and $n$ denotes the Freundlich exponent that has an association with adsorption capacity and the adsorption intensity, respectively [33]. Figure 14 shows the

Freundlich model isotherm fit for the studied data. The most suitable Freundlich constant value of the $n$ remains between 1 and 10 in most of the adsorption studies (Table 1). The value of $n$ is estimated to be 3.795, thereby portraying that the sorption is favorable.

Upon comparing both isotherms, the Langmuir isotherm model is inferred as the adsorption followed the monolayer mode of adsorption. Further, it also indicates that the adsorbent's surface remains homogenous. The maximum adsorption capacity as per estimation was 195.54 mg·g$^{-1}$.

*3.4. Adsorption Kinetics.* Kinetic models are utilized most of the time to evaluate the rate of adsorption process. In the current study, the kinetic data for different types of adsorbate-adsorbent systems were evaluated based on two different kinetic models such as the pseudo-first-order [34] and pseudo-second-order [35].

Pseudo-first-order kinetic model:

$$\log \; (q_e - q_t) = \log \; q_e - \frac{k_1}{2.303} \; t, \qquad (4)$$

where $q_t$ is the adsorption capacity at time $t$ (mg/g), $k_1$ is the pseudo-first-order rate constant (min$^{-1}$), and $t$ is the time (min).

Pseudo-second-order kinetic model:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t. \qquad (5)$$

$k_2$ is the pseudo-second-order rate constant (g/mg/min), and $h = k_2 \cdot q_e^2$ is the initial adsorption rate (mg/g/min).

The kinetic analysis for the current study is shown in Figures 15 and 16. Table 2 lists the kinetic results in which the pseudo-first-order remains the best fit instead of the pseudo-second-order kinetic model. This infers that physical adsorption is the rate-controlling step for the removal of chromium (VI) ions from the aqueous solution to the adsorbent surface.

*3.5. Performance Comparison of Various Adsorbents for Chromium Removal.* The various adsorbents utilized to remove the chromium from aqueous solution are listed in Table 3. The optimum conditions and their removal efficiency/adsorption capacity are given in Table 3. The prepared adsorbent from the current research showed the higher adsorption capacity as compared to other reported adsorbents.

# 4. Conclusion

Aged refuse, the solid waste material that is abundantly available in dumping sites, can be used in removal of chromium (VI) from aqueous solution. In this study, the aged refuse was modified by acid washing method and was validated as an adsorbent. The FTIR spectrum inferred that adequate functional groups are available on the adsorbent surface for the removal of chromium (VI) ions from aqueous solution. The surface properties of the aged refuse were improved after its treatment with sulphuric acid. Batch studies were conducted at RT by varying the parameters such as pH, dosages, initial chromium (VI) ion concentration, and time. At an optimized condition, the Langmuir adsorption capacity of 195.54 mg/g was observed. The Langmuir model is comparatively well correlated than the Freundlich model which indicates that the adsorbent possessed a homogeneous adsorbent surface which leads to monolayer adsorption of chromium (VI) ions over the acid-treated aged refuse. The optimized condition on the removal of chromium (VI) ions by the acid-treated aged refuse was pH of 3.0, adsorbent dose of 1.5 g/L, temperature of 30°C, and at a contact time of 60 min. Pseudo-first-order kinetic model is deemed to be the best model than the pseudo-second-order which indicates that the physisorption is the rate-controlling step. To conclude, aged refuse can be recommended as a viable adsorbent for the removal of chromium (VI) ions from the aqueous solution.

# Abbreviations

FTIR:   Fourier transform infrared spectroscopy
XRD:    X-ray diffraction
SEM:    Scanning electron microscope
EDAX:   Energy dispersive X-ray analysis
BET:    Brunauer-Emmett-Teller analysis
TGA:    Thermogravimetric analysis
WHO:    World Health Organization
RT:     Room temperature
AAS:    Atomic absorption spectroscopy.

# Data Availability

Data are available on request.

# Conflicts of Interest

The authors declare that they have no conflicts of interest.

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