Removal of chromium (VI) from aqueous solution by chemically modified gingelly oil cake carbon

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An activated carbon is prepared from gingelly oil cake (GOC) by using sulphuric acid treatment and its Cr(VI) removal capacity is compared with that of commercial activated carbon (CAC). The effect of experimental parameters such as pH, initial concentration, contact time and adsorbents dose for Cr(VI) removal are studied. Langmuir, Freundlich and Temkin models are tested to describe the equilibrium isotherms. The maximum adsorption capacity of the adsorbents calculated from Langmuir isotherm is found to be 30.58 mg/g and 25.13 mg/g for sulphuric acid treated gingelly oil cake carbon (STGOC) and CAC respectively. \textit{R}^2 values show that both Langmuir and Freundlich models fit well to explain the adsorption phenomenon for STGOC and CAC. The kinetic data fits best to pseudo second-order model. FTIR analysis is used to obtain information on the nature of possible interaction between adsorbents and metal ions. SEM images confirmed the adsorption of Cr(VI) onto these adsorbents through morphological observations. Gibbs free energy values showed the feasibility of process and spontaneous nature of the adsorption. The adsorbents are also tested for the removal of Cr(VI) from chrome plating wastewater and found to remove Cr(VI) effectively.

\textbf{Keywords:} Cr(VI) removal, Gingelly oil cake carbon, CAC, Adsorption isotherms, Kinetics, Chrome plating wastewater

Hexavalent chromium is a highly toxic metal that is carcinogenic, mutagenic and teratogenic to living organisms\textsuperscript{1}. Cr(VI) exists mainly in the anionic forms of chromate and dichromate in aqueous systems and is released from various industrial operations such as leather tanning and metallurgy\textsuperscript{2}. Cr(VI) containing wastewater from these processes is disposed by means of domestic sewage systems with little treatment in some underdeveloped areas. The recommended limit of Cr(VI) in potable water\textsuperscript{3} is only 0.05 mg/L. A variety of methods have been developed for the removal of Cr(VI) from wastewater, such as ion-exchange, chemical precipitation, electro-deposition and reverse osmosis\textsuperscript{4,5}. But these methods suffer from disadvantages such as, requiring large excess of chemicals, generating volumetric sludges, involving high capital investment and running cost. Adsorption is one of the techniques that would be comparatively more useful and economical for this aim\textsuperscript{6}. Several adsorption methods have been developed and tested, ranging from low cost waste material, such as: moss peat\textsuperscript{7}, sawdust\textsuperscript{8}, hazelnut shell\textsuperscript{9}, rice husk carbon\textsuperscript{10}, to more sophisticated adsorbents, such as modified clay\textsuperscript{11}, modified steel slag\textsuperscript{12}, nanoscale magnetic material\textsuperscript{13} and chitosan based composite\textsuperscript{14} for the treatment of Cr(VI) metal since the commercial activated carbon is expensive.

The objective of the present study is to investigate the adsorption potential of carbon derived from gingelly oil cake by chemical modification for the removal of Cr(VI) from aqueous solution and synthetic chrome plating wastewater and compare the performance of the carbon with commercial activated carbon. The optimum adsorption conditions were evaluated as a function of contact time, pH, adsorbent dose and initial concentration. Adsorption isotherm, kinetic studies and desorption studies were also conducted to understand the adsorption phenomenon.

\textbf{Experimental Procedure}

\textbf{Instrumentation}

The Fourier transform infrared spectroscopy (FTIR) spectrum was recorded with an IR spectrometer, (Model: 8400S, SHIMADZU, Japan). Surface morphology was studied by using scanning electron microscope (Model: JEOL 6360, Japan). The atomic absorption spectrometer (AAS) (Model: SL

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163, ELICO Ltd, Hyderabad, India), was used for the determination of Cr(VI) concentration. Adsorbents were analysed using sequential X-ray fluorescence spectrometer (XRF) (Model: ARL-Advant XP, Thermo Electron Corporation, Switzerland), carbon and sulphur analyzer (Model: LECO CS-200) and nitrogen and oxygen analyzer (Model: LECO TC-500) (LECO Corporation, Michigan, USA). Nitrogen adsorption-desorption isotherms were measured on a surface and porosimetry analyzer (Model: Micromeritics ASAP 2020, USA). The pH was measured with a digital pH meter (Model: 335, Systronics, India). A thermally controlled mechanical shaker (horizontal shaking type) with a speed of 200 rpm was used for batch studies.

Reagents
All the chemicals used in this study were of analytical reagent grade and distilled water was used for the preparation of solutions.

Preparation of Cr(VI) solutions
Stock aqueous solution of Cr(VI) having concentration of 1000 mg/L was prepared by dissolving 2.829 g of K₂Cr₂O₇ in 100 mL of distilled water and quantitatively diluting to 1000 mL using distilled water. Cr(VI) solutions of desired concentrations were prepared by adequate dilution of the stock solution with distilled water.

Preparation of adsorbents
Gingelly oil cake, a waste material procured from oil industries, was washed several times with distilled water to remove any surface impurities and dried. 50 g of dried oil cake was mixed with 200 g (1:4 ratio by wt) of concentrated sulphuric acid. The mixing was done by adding small quantities of oil cake to acid taken in 1000 mL beaker with vigorous stirring. Charring of the cake occurs immediately accompanied by evolution of heat and fumes. When the reaction subsides, the mixture was left in air oven at 140-160°C for a period of 24 h. The carbonized material was then washed with approximately 4.0-4.5 L of distilled water to remove free sulphuric acid and dried at 110°C.

Sulphuric acid treated gingelly oil cake carbon (STGOC) and commercial activated carbon (CAC) (SD fine chem., Mumbai, India) procured from the market were powdered and sieved to a particle size of 80-120 mesh (ASTM) and used for further experiments.

Batch experiments
In all sets of experiments, 100 mL of Cr(VI) solution with desired concentration adjusted to a desired pH, were taken in high density poly(ethylene) (HDPE) bottles of 300 mL capacity and desired dose of adsorbent was added to it. The solution pH was adjusted with 0.1 M HNO₃ or KOH. The solutions were agitated for various contact times at 30±1°C and carbon particles were separated by using centrifuge with a speed of 500 rpm and the supernatant liquid was analysed for Cr(VI) by AAS. Solute and adsorbent free blanks were used to control in all the experiments. Adsorption isotherm and kinetic studies were carried out with different initial concentrations of Cr(VI) by maintaining a constant adsorbent dose. Adsorption isotherm studies were made after equilibrating the solution for 24 h. The concentration of unadsorbed Cr(VI) in the supernatant liquid was determined by using an AAS with an air-acetylene flame. The hollow cathode lamp was operated at 15 mA and analytical wavelength was set at 358 nm. The removal efficiency (E) of the adsorbents on Cr(VI) was calculated by using the following expression.

\[ E(\%) = \left(1 - \frac{C_e}{C_o}\right) \times 100 \quad \ldots (1) \]

where, \( C_o \) and \( C_e \) are the initial and equilibrium concentrations (mg/L) of Cr(VI) solution.

Results and Discussion
Properties of adsorbents
Tables 1 and 2 show the proximate analysis, characteristics and XRF analysis of STGOC and CAC. Proximate analysis was carried out according to Indian Standard Methods of Tests[1]. The low pH value of STGOC is due to sulphuric acid treatment. The high decolorizing power and low phenol number values suggest that CAC may be more suitable for organic adsorption than STGOC. The higher surface area of CAC is mainly due to high temperature carbonization adopted for the preparation of CAC than STGOC. The low surface area of STGOC is compensated by its high ion-exchange capacity and higher average pore size in the removal of chromium ions from solutions. Though the carbon content of STGOC is lesser than CAC, its Cr(VI) removal capacity has been found to be more, which may be due to the presence of various functional groups.
The high values of sulphur, nitrogen and oxygen content in STGOC, shows that these elements are present in the functional groups, favoring Cr(VI) removal from solutions. Loss on ignition (LOI) (Table 2) corresponds to carbon content and other volatile materials. The oxides of sulphur are higher in STGOC than CAC, due to the introduction of sulphonic acid groups by sulphuric acid treatment.

**Effect of contact time**

Contact time of adsorbate and adsorbent is of great importance in adsorption, because it depends on the nature of the system used. The adsorption of Cr(VI) onto these adsorbents was initially very fast and slowly reached equilibrium (Fig. 1). Thus, 120 min and 180 min contact time were considered to be adequate for the adsorption of Cr(VI) onto STGOC and CAC respectively. The removal efficiency by STGOC for an initial Cr(VI) concentration of 10 mg/L and for a sorbent dose of 0.2 g/100 mL, for an optimum time of 2 h at pH 2.5, is 96.0% (48.0 mg/g), whereas, the removal efficiency by CAC for a sorbent dose of 0.3 g/100 mL, for an optimum time of 3 h at pH 1.5, is 88.5% (29.5 mg/g). This shows that, with respect to contact time, the removal efficiency of STGOC is 1.5 times more than that of CAC.

Initially, active binding sites were largely available on these sorbents surfaces and consequently the rates of adsorption for these sorbents were high. However, with increasing coverage, the fraction of the surface rapidly diminished and Cr(VI) ions had to compete among themselves for the adsorption sites.

**Effect of pH**

Aqueous phase pH governs the speciation of metals and also the dissociation of active functional sites on the sorbent. Hence, metal sorption is critically linked with pH. Not only different metals show different pH optima for their sorption but may also vary from one kind of biomass to the other. It can be observed from Fig. 2 that the uptake of Cr(VI) increases with decrease in pH. For an initial concentration of 10 mg/L and for a carbon dose of 0.2 g/100 mL, the maximum removal achieved by STGOC at pH 2.5 is 95.8% (47.9 mg/g), whereas, for a carbon dose of

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**Table 1—Physico-chemical characteristics of the activated carbons**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>STGOC (%)</th>
<th>CAC (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture (%)</td>
<td>2.30</td>
<td>3.70</td>
</tr>
<tr>
<td>Matter soluble in water (%)</td>
<td>0.84</td>
<td>4.80</td>
</tr>
<tr>
<td>Matter soluble in acid(%)</td>
<td>4.90</td>
<td>9.20</td>
</tr>
<tr>
<td>Bulk density (g/cm³)</td>
<td>0.79</td>
<td>0.74</td>
</tr>
<tr>
<td>pH</td>
<td>3.70</td>
<td>7.60</td>
</tr>
<tr>
<td>Iron content (%)</td>
<td>0.28</td>
<td>0.18</td>
</tr>
<tr>
<td>Decolorizing power (mg/g)</td>
<td>33.10</td>
<td>90.00</td>
</tr>
<tr>
<td>Ion-exchange capacity (m equiv/g)</td>
<td>0.72</td>
<td>Nil</td>
</tr>
<tr>
<td>Phenol number (mg)</td>
<td>57.00</td>
<td>35.00</td>
</tr>
<tr>
<td>Ash (%)</td>
<td>4.95</td>
<td>1.19</td>
</tr>
</tbody>
</table>

**Adsorption-desorption isotherm:**

- BET surface area (m²/g) 6.78 558.02
- Langmuir surface area (m²/g) 15.37 798.15
- Total pore volume (cm³/g) 0.02 0.32
- Average pore size (Å) 89.56 22.88

**Elemental analysis**

| Carbon(%) | 53.42 | 85.90 |
| Sulphur(%) | 3.26 | 0.22 |
| Nitrogen(%) | 2.72 | 0.11 |
| Oxygen(%) | 15.59 | 4.99 |

**Table 2—XRF analysis of adsorbents**

<table>
<thead>
<tr>
<th>Component</th>
<th>STGOC (%)</th>
<th>CAC (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loss on Ignition</td>
<td>93.172</td>
<td>98.430</td>
</tr>
<tr>
<td>CaO</td>
<td>0.480</td>
<td>0.183</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.012</td>
<td>0.008</td>
</tr>
<tr>
<td>K₃O</td>
<td>0.009</td>
<td>0.042</td>
</tr>
<tr>
<td>MgO</td>
<td>0.096</td>
<td>0.032</td>
</tr>
<tr>
<td>SO₃</td>
<td>4.160</td>
<td>0.159</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.410</td>
<td>0.161</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1.532</td>
<td>0.870</td>
</tr>
<tr>
<td>Cl</td>
<td>0.006</td>
<td>0.007</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.114</td>
<td>0.063</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.006</td>
<td>0.064</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>MnO</td>
<td>0.005</td>
<td>0.002</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.007</td>
<td>0.002</td>
</tr>
<tr>
<td>CuO</td>
<td>0.001</td>
<td>0.005</td>
</tr>
</tbody>
</table>

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Fig. 1—Effect of agitation time on adsorption of Cr(VI)
0.3 g/100 mL, the maximum removal achieved by CAC at pH 1.5 is 88.5% (29.5 mg/g). A lower pH causes the adsorbent surface to carry a more positive charge and thus would more significantly attract the negatively charged chromium species in solution. This indicates that the physicochemical adsorption due to coulombic attraction was the predominant process of Cr(VI) removal. When the pH of the solution increases, the surface becomes negatively charged and the adsorption capacity for Cr(VI) decreases as negatively charged sites on the adsorbent surface does not favor Cr(VI) due to electrostatic repulsion. Chromium exists mainly in two oxidation states which are Cr(VI) and Cr(III) and the stability of these forms is dependent on the pH of the system. It is well known that, HCrO$_4^-$ is the dominant form of Cr(VI) at pH below 3.0. Maximum adsorption at pH 2.5 and 1.5 for STGOC and CAC indicates that Cr(VI) is the predominant species adsorbed on the STGOC and CAC at pH 2.5 and 1.5 respectively.

**Effect of adsorbent dose**

The effect of adsorbent dose on the percentage removal of Cr(VI) for these adsorbents is shown in Fig. 3. A maximum removal of Cr(VI) achieved by STGOC at an optimum sorbent dose of 0.2 g/100 mL for an initial concentration of 10 mg/L at pH 2.5 is 95.8% (47.9 mg/g), whereas, the maximum removal by CAC at an optimum sorbent dose of 0.3 g/100 mL and at a pH of 1.5 is 88.2% (29.4 mg/g). It could be seen from the figure that initially the percentage removal increases very sharply with the increase in adsorbent dose but after a certain value (0.2 g/100 mL for STGOC and 0.3 g/100 mL for CAC) the percentage removal was almost constant. This trend is expected because as the adsorbent dose increases the number of adsorbent particles increases and thus more Cr(VI) is attached to their surfaces.

**Adsorption isotherms**

Nitrogen adsorption-desorption isotherms of STGOC and CAC are also carried out to understand the type of adsorption and are illustrated in Figs 4 and 5. According to IUPAC classification, the adsorption isotherm of STGOC has type III shape with H3 hysteresis loop. The convexity of isotherm to the pressure axis suggests co-operative adsorption, which means that the already adsorbed molecules tend to enhance the adsorption of other molecules. In this type of isotherm, adsorbent-adsorbate interactions are less important than adsorbate-adsorbate interactions. Weak adsorbent-adsorbate interactions result in small adsorption at lower relative pressure. The hysteresis loop of this isotherm is associated with filling and emptying of the mesopores by capillary condensation. The type H3
loop, which does not exhibit any limiting adsorption at high
\( p/p_0 \), is adsorbed with aggregates of plate-like
particles giving rise to slit-shaped pores\(^{25}\).

According to the IUPAC classification, the
adsorption isotherm on CAC has type I shape with
H4 hysteresis loop. It shows a horizontal plateau
parallel to pressure axis. Adsorption at higher relative
pressures is small and tending to level off. Type I
isotherm is mostly common to chemisorption, as
pores being narrow that they cannot accommodate
more than a single molecular layer. Nitrogen uptake
was significant only in the low pressure region
(region I) where \( p/p_0 < 0.1 \) indicating CAC was
typically micro porous. The type H4 loop is often
associated with narrow slit-like pores\(^{25}\).

Adsorption isotherm can be used to describe how
solute interacts with adsorbents and so are critical in
optimizing the use of adsorbents. The commonly used
isotherms, the Langmuir, Freundlich and Temkin
have been applied for this study. The linear form of
Langmuir equation is given as\(^{26}\).

\[
\frac{1}{q_e} = \frac{1}{b} + \frac{1}{a b C_e} \quad \ldots(2)
\]

where, \( C_e \) is the equilibrium concentration (mg/L), \( q_e \)
is the amount adsorbed at equilibrium (mg/g) and \( a \) and \( b \) are Langmuir constants related to
energy of adsorption (L/mg) and adsorption capacity
(mg/g) respectively. The plot of \( 1/q_e \) versus \( 1/C_e \)
gives a straight line. Figure 6 shows, Langmuir
adsorption isotherm for adsorption of Cr(VI) onto
STGOC and CAC after an equilibration time of
24 h. Langmuir constants, \( a \) and \( b \) were determined
from the slopes and intercepts and the values are
given in Table 3.

A dimensionless constant, separation factor (\( R_L \))
can be used to predict whether a sorption system is
favorable or unfavorable in batch adsorption process.\(^{26}\)
\( R_L \) values between 0 and 1 represent favorable
isotherm. \( R_L \) was calculated from Langmuir isotherm
based equation.

\[
R_L = \frac{1}{(1 + aC_o)} \quad \ldots(3)
\]

where, \( C_o \) is the initial concentration of Cr(VI) and
\( a \) is the Langmuir constant.

The parameter, \( R_L \) indicates the nature of
adsorption process as given below;
- \( R_L > 1 \) = unfavorable isotherm
- \( R_L = 1 \) = linear isotherm
- \( R_L = 0 \) = irreversible isotherm
- \( 0 < R_L < 1 \) = favorable isotherm

The \( R_L \) values were found to be between 0 and 1
for STGOC and CAC showing the sorption of Cr(VI)
on these adsorbents is favorable. From \( R_L \) values of
Table 3, it is clear that the sorption process was
favorable for Cr(VI) removal for these adsorbents at
all concentrations investigated.

The linear form of Freundlich isotherm is
represented by the following equation\(^{27}\).

\[
\log \frac{x}{m} = \log K_F + \frac{1}{n} \log C_e \quad \ldots(4)
\]

where \( C_e \) is the equilibrium concentration (mg/L)
and \( x/m \) is the amount adsorbed per unit weight
of adsorbent. The plot of \( \log(x/m) \) versus \( \log C_e \)
gives a straight line. Figure 7 shows Freundlich
isotherm for adsorption of Cr(VI) onto

\[
\begin{array}{|c|c|c|c|}
\hline
\text{Adsorbent} & \text{ } a \text{ } & \text{ } b \text{ } & \text{ } R_L \text{ } & \text{ } R^2 \text{ } \\
\hline
\text{STGOC} & 0.1080 & 30.58 & 0.2517 & 0.9746 \\
\text{CAC} & 0.0822 & 25.13 & 0.3020 & 0.9799 \\
\hline
\end{array}
\]

Table 3—Langmuir adsorption isotherm constants for adsorbents

Fig. 5—Nitrogen adsorption-desorption isotherm of CAC

Fig. 6—Langmuir adsorption isotherm for adsorption of Cr(VI)
on STGOC & CAC
adsorption isotherms for adsorption of Cr(VI) onto STGOC and CAC. The $K_F$ and $n$ values were calculated from the intercepts and slopes, respectively. The values of adsorption capacity ($K_F$), adsorption intensity ($n$) and correlation coefficient ($R^2$) for various adsorbents are given in Table 4. The values of $1<n<10$ show favorable adsorption of Cr(VI) onto these adsorbents.

The Langmuir adsorption capacity of STGOC has been found to be comparatively higher than that of CAC (Table 3). But, the BET isotherm studies indicate that the surface area of STGOC is much lesser than CAC (Table 1). This could be due to the following reasons: (i) though the surface area of STGOC is lesser, it is compensated by larger average pore sizes, much higher than that of CAC, which may enhance the diffusion of Cr(VI) ions and thereby increasing the adsorption capacity of STGOC; (ii) in addition to the high ion-exchange capacity of STGOC, the introduction of -SO$_3$H and -SO$_4$H groups by sulphuric acid treatment also contributes to its adsorption capacity; (iii) moreover STGOC exhibit type III shape with H3 hysteresis loop, suggesting co-operative isotherm, which enhances the adsorption of other Cr(VI) ions; and (iv) the participation of functional groups such as -SO$_3$H and -SO$_4$H in Cr(VI) adsorption is also evidenced by shifts in frequencies corresponding to these groups in FTIR spectra of STGOC before and after Cr(VI) adsorption.

In order to find out the applicability of Temkin isotherm to the adsorption process, the experimental data were applied to Temkin isotherm model.

The linear form of Temkin isotherm is represented by the following equation:

$$q_e = a_t + 2.3 b_t \log C_e$$

where $C_e$ is the equilibrium concentration (mg/L) and $q_e$ is the amount adsorbed per unit weight of adsorbent. The values of $a_t$ (mg/g) and $b_t$ (L/mg) were obtained by plotting adsorption capacity and equilibrium concentration. The plot of $q_e$ versus log $C_e$ gives a straight line. Figure 8 shows Temkin adsorption isotherm for adsorption of Cr(VI) onto STGOC and CAC. The values of $a_t$ and $b_t$ calculated from the intercepts, slopes respectively and $R^2$ values are shown in Table 5.

Correlation coefficient ($R^2$) values were calculated by using statistical analysis to determine suitable isotherm model. $R^2$ is a measure of goodness-of-fit. The fit is better when the $R^2$ value is close to unity. Hence, $R^2$ values were determined for the linear plots obtained for the three isotherm models and are shown in Tables 3-5. Though both Langmuir and Freundlich adsorption isotherms fit well with experimental data, it may be concluded from $R^2$ values that Freundlich isotherm model fits best to both STGOC and CAC as these values are very close to unity.

### Table 4—Freundlich adsorption isotherm constants for adsorbents

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>$K_F$ (mg/g)</th>
<th>$n$ (L/mg)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>STGOC</td>
<td>1.433</td>
<td>1.567</td>
<td>0.9946</td>
</tr>
<tr>
<td>CAC</td>
<td>1.447</td>
<td>1.644</td>
<td>0.9954</td>
</tr>
</tbody>
</table>

### Table 5—Temkin adsorption isotherm constants for adsorbents

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>$a_t$ (mg/g)</th>
<th>$b_t$ (L/mg)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>STGOC</td>
<td>10.757</td>
<td>18.6326</td>
<td>0.9557</td>
</tr>
<tr>
<td>CAC</td>
<td>0.9542</td>
<td>17.165</td>
<td>18.2048</td>
</tr>
</tbody>
</table>

Fig. 7—Freundlich adsorption isotherm for adsorption of Cr(VI) onto STGOC & CAC

Fig. 8—Temkin adsorption isotherm for adsorption of Cr(VI) onto STGOC & CAC
Adsorption kinetics

In order to clarify the adsorption kinetics of Cr(VI) ions onto these adsorbents, two kinetic models, such as Lagergren’s pseudo-first order and pseudo-second order models were applied to the experimental data.

The linearised form of the pseudo-first order rate equation of Lagergren is given as:

\[ \ln \left( q_{e\text{ (exp)}} - q_{t\text{ (exp)}} \right) = \ln q_{e\text{ (theo)}} - k_1 t \]

where, \( q_{e\text{ (exp)}} \) and \( q_{t\text{ (exp)}} \) are the amount of the metal ions adsorbed (mg/g) at equilibrium and at time \( t \) (min), respectively and \( k_1 \) is the pseudo-first order equilibrium rate constant (min\(^{-1}\)). A plot of \( \ln \left( q_{e\text{ (exp)}} - q_{t\text{ (exp)}} \right) \) versus \( t \) gives a straight line with slope of \( k_1 \) and an intercept of \( \ln q_{e\text{ (theo)}} \). The straight line nature of curve shows the applicability of pseudo-first order rate equation. Figures 9 and 10 show pseudo first-order kinetics for the adsorption of Cr(VI) onto STGOC and CAC, respectively.

The pseudo-second order rate equation may be expressed as:

\[ \frac{t}{q_{t\text{ (exp)}}} = \frac{1}{k_2 q_{e\text{ (theo)}}^2} + \frac{t}{q_{e\text{ (theo)}}} \]

where \( k_2 \) is the pseudo-second order adsorption rate constant (g/mg min\(^{-1}\)). A plot of \( \left( \frac{t}{q_{t\text{ (exp)}}} \right) \) versus \( t \) also produces straight line with slope of \( 1/q_{e\text{ (theo)}} \) and intercept of \( 1/k_2 q_{e\text{ (theo)}} \). It indicates the applicability of pseudo-second order model. Figs. 11 and 12 show, pseudo second order kinetics for the adsorption of Cr(VI) onto STGOC and CAC respectively.

In order to compare quantitatively the applicability of kinetic models in fitting to data, the percent relative deviation (\( P \)), was calculated as per the following expression:

\[ P = \frac{100}{N} \sum \left( \frac{q_{e\text{ (exp)}} - q_{e\text{ (theo)}}}{q_{e\text{ (exp)}}} \right) \]

Fig. 9—Pseudo first order kinetics for the adsorption of Cr(VI) onto STGOC

Fig. 10—Pseudo first-order kinetics for the adsorption of Cr(VI) onto CAC

Fig. 11—Pseudo second-order kinetics for the adsorption of Cr(VI) onto STGOC

Fig. 12—Pseudo second-order kinetics for the adsorption of Cr(VI) onto CAC
where, \( q_{e\text{ (exp)}} \) is the experimental value of \( q_e \) at any value of \( C_e \), \( q_{e \text{ (theo)}} \) is the corresponding theoretical value of \( q_e \) and \( N \) is the number of observations. It is found that lower the value of percentage deviation \( (P) \) better is the fit. It is generally accepted that when \( P \) value is less than 5, the fit is considered to be excellent.\(^{31}\) The results have been analyzed using Eqs (6) and (7). The experimental data fit well in both the equations. The values of \( q_{e \text{ (theo)}} \) calculated from these models are compared with experimental values \( q_{e \text{ (exp)}} \) and are shown in Table 6. It was found that values of \( q_{e \text{ (theo)}} \) calculated from the pseudo-first order kinetic model differed appreciably from the experimental values \( q_{e \text{ (exp)}} \). The percent relative deviation \( (P) \) was also very high. On the other hand, values of \( q_{e \text{ (theo)}} \) are found to be very close to \( q_{e \text{ (exp)}} \) when pseudo-second order rate equation was applied. The percent relative deviation \( (P) \) is well within the range and also the values of correlation coefficients \( (R^2) \) are close to unity in pseudo-second order kinetics. These results indicate that the adsorption of Cr(VI) onto these adsorbents is governed by pseudo-second order kinetics predominantly.

Gibbs free energy of adsorption \((\Delta G^0_{\text{ads}})\)

In order to understand whether the adsorption process is spontaneous or non-spontaneous, the value of free energy of adsorption \((\Delta G^0_{\text{ads}})\) is calculated by the following equation,

\[
\Delta G^0_{\text{ads}} = -RT \ln a \quad \ldots (9)
\]

where \( R \) is the universal gas constant \((8.314 \text{ J mol}^{-1}\text{K}^{-1})\), \( T \) is the absolute temperature \((\text{K})\) and \( a \) is the Langmuir constant. Gibbs free energy change \(\Delta G^0_{\text{ads}}\) of various adsorbents is shown in Table 7. The values of \(\Delta G^0_{\text{ads}}\) have been found to be negative for both the adsorbents indicating the feasibility and spontaneous nature of adsorption.

### Diffusion mechanism

Weber-Morris intra-particle diffusion model

In order to examine the applicability of Weber-Morris intra-particle diffusion model, adsorption kinetic data was characterized using the relationship between specific sorption \((q_t)\) and square root of time \((t^{1/2})\) as shown in Eq. (10).

\[
q_t = K_{id} t^{1/2} \quad \ldots (10)
\]

where \(q_t\) is the amount adsorbed per unit mass of the adsorbent \((\text{mg/g})\) at time \( t \) and \( K_{id} \) is the intra-particle diffusion constant \((\text{mg/g/min}^{1/2})\). If the intra-particle diffusion is involved in the adsorption process, then a plot of the amount of chromium (VI) adsorbed per unit mass of the adsorbent \((q_t)\) against square root of time \((t^{1/2})\) gives a straight line curve and the particle diffusion would be the rate controlling step if this line passes through the origin.\(^{32,33}\) Such plots may also represent multi-linearity, indicating that two or more steps are involved in the adsorption process. In a multi-linear curve the first sharper portion is attributed to the distribution of adsorbate through the solution to the external surface of adsorbent or the boundary layer diffusion of solute molecules or ions. The second portion describes the gradual adsorption stage, where intraparticle diffusion is rate limiting. The third portion is attributed to the final equilibrium stage where intraparticle diffusion starts to slow down due to extremely low adsorbate concentrations in the solution.\(^{34}\)

The plot of \(q_t\) versus \(t^{1/2}\) for the adsorption of Cr(VI) onto STGOC and CAC are presented in Figs 13 and 14, respectively. It could be seen that these plots are not linear over the given time range, implying that more than one process may be involved in Cr(VI) adsorption. Furthermore, the curves are not

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Conc. (mg/L)</th>
<th>Pseudo-first-order kinetics</th>
<th>Pseudo-second-order kinetics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \begin{array}{c} k_1 \text{ (1/min)} \ q_{e \text{ (theo)}} \text{ (mg/g)} \end{array} )</td>
<td>( \begin{array}{c} q_{e \text{ (exp)}} \text{ (mg/g)} \end{array} )</td>
<td>( \begin{array}{c} R^2 \ q_{e \text{ (theo)}} \text{ (mg/g)} \end{array} )</td>
</tr>
<tr>
<td>STGOC</td>
<td>10</td>
<td>0.0277 1.7856 9.60 0.9568</td>
<td>81.40 0.0099 10.0301 9.60 0.9991 4.4801</td>
</tr>
<tr>
<td>STGOC</td>
<td>7</td>
<td>0.0277 1.2981 6.60 0.9489</td>
<td>80.33 0.0289 6.8493 6.60 0.9994 3.7775</td>
</tr>
<tr>
<td>STGOC</td>
<td>5</td>
<td>0.0298 1.1862 4.60 0.9642</td>
<td>74.21 0.0179 4.8239 4.60 0.9993 4.8680</td>
</tr>
<tr>
<td>STGOC</td>
<td>3</td>
<td>0.0223 0.6792 2.60 0.9706</td>
<td>73.88 0.0175 2.8153 2.60 0.9987 8.2814</td>
</tr>
<tr>
<td>CAC</td>
<td>10</td>
<td>0.0303 1.2930 8.85 0.9766</td>
<td>85.39 0.0177 9.1324 8.85 0.9996 3.1912</td>
</tr>
<tr>
<td>CAC</td>
<td>7</td>
<td>0.0406 1.5356 6.00 0.9750</td>
<td>74.40 0.0371 6.2972 6.00 0.9990 4.9538</td>
</tr>
<tr>
<td>CAC</td>
<td>5</td>
<td>0.0513 1.2954 4.25 0.9591</td>
<td>69.52 0.0271 4.4523 4.25 0.9982 4.7614</td>
</tr>
<tr>
<td>CAC</td>
<td>3</td>
<td>0.0416 0.4348 2.35 0.9618</td>
<td>81.50 0.0507 2.4558 2.35 0.9989 4.5019</td>
</tr>
</tbody>
</table>
passing through the origin in both the cases, implying that intra-particle diffusion was not the only rate-controlling step in the removal of Cr(VI)\(^{35}\). The values of \(K_d\) at different concentrations were calculated from the slopes of these plots and are presented in Table 8.

**Film and pore diffusion coefficients**

In an adsorption process, if film diffusion were to be the rate determining step, then the value of film diffusion coefficient \((D_f)\) be in the order of \(10^{-6}-10^{-8}\) cm\(^2\)/s and if pore diffusion were to be the rate-limiting factor, the pore diffusion coefficient \((D_p)\) be in the order of \(10^{-11}-10^{-13}\) cm\(^2\)/s \(^{36}\).

In order to find out the nature of the process responsible for the adsorption of chromium(VI) onto STGOC and CAC, film and pore diffusion coefficients were calculated by using pseudo second-order overall rate constant values. Assuming the spherical geometry for the sorbents, the \(t_{1/2}\) values could be calculated for each concentration by substituting the corresponding second-order overall rate constant of the reaction in the following expression.

\[
t_{1/2} = \frac{1}{ak_2} \quad \ldots \quad (11)
\]

where \(a\) is the initial concentration of chromium(VI) and \(k_2\) is the pseudo-second order constant. \(D_p\) and \(D_f\) could then be calculated using the Eqs (12) and (13).

Knowing the average diameter of the particles and taking the film thicknesses as \(10^{-3}\) cm as reported by Helffrich\(^{37}\).

\[
t_{1/2} = 0.03 \frac{r_o^2}{D_p} \quad \ldots \quad (12)
\]

\[
t_{1/2} = 0.23 \frac{r_od}{D_f} \quad \ldots \quad (13)
\]

where \(r_o\) is radius of the sorbent (cm), \(D_p\) is pore diffusion coefficient (cm\(^2\)/s), \(D_f\) is film diffusion co-efficient (cm\(^2\)/s), \(c/\bar{c}\) is equilibrium loading of the sorbent and \(t_{1/2}\) is half-life period (s).

Since the carbon particles of STGOC and CAC used are of the size range of 80-120 mesh (ASTM), the average diameter of the carbon particles is taken as 0.152 mm. Using this value, the film diffusion and pore diffusion coefficients are calculated and given in

### Table 7—Gibbs free energy of adsorption for adsorbents

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>(a) (L/mg)</th>
<th>(\Delta G_{\text{ads}}) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>STGOC</td>
<td>0.1081</td>
<td>-21.75</td>
</tr>
<tr>
<td>CAC</td>
<td>0.0822</td>
<td>-21.06</td>
</tr>
</tbody>
</table>

### Table 8—Diffusion coefficients of the adsorbents for the removal of Cr(VI)

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Conc. (mg/L)</th>
<th>Intraparticle diffusion coefficient (K_d) (mg/g/min(^{1/2}))</th>
<th>Film diffusion coefficient (D_f) (cm(^2)/s)</th>
<th>Pore diffusion coefficient (D_p) (cm(^2)/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>STGOC</td>
<td>10</td>
<td>8.03 \times 10(^{-2})</td>
<td>9.8090 \times 10(^{-8})</td>
<td>1.0129 \times 10(^{-9})</td>
</tr>
<tr>
<td>STGOC</td>
<td>7</td>
<td>5.91 \times 10(^{-2})</td>
<td>1.6557 \times 10(^{-7})</td>
<td>1.7408 \times 10(^{-9})</td>
</tr>
<tr>
<td>STGOC</td>
<td>5</td>
<td>3.74 \times 10(^{-2})</td>
<td>1.8539 \times 10(^{-7})</td>
<td>1.9976 \times 10(^{-9})</td>
</tr>
<tr>
<td>STGOC</td>
<td>3</td>
<td>4.13 \times 10(^{-2})</td>
<td>1.7223 \times 10(^{-7})</td>
<td>1.9699 \times 10(^{-9})</td>
</tr>
<tr>
<td>CAC</td>
<td>10</td>
<td>8.76 \times 10(^{-2})</td>
<td>1.0994 \times 10(^{-7})</td>
<td>1.2314 \times 10(^{-9})</td>
</tr>
<tr>
<td>CAC</td>
<td>7</td>
<td>7.47 \times 10(^{-2})</td>
<td>1.0305 \times 10(^{-7})</td>
<td>1.1918 \times 10(^{-9})</td>
</tr>
<tr>
<td>CAC</td>
<td>5</td>
<td>2.35 \times 10(^{-2})</td>
<td>1.6150 \times 10(^{-7})</td>
<td>1.8834 \times 10(^{-9})</td>
</tr>
<tr>
<td>CAC</td>
<td>3</td>
<td>1.67 \times 10(^{-2})</td>
<td>2.7817 \times 10(^{-7})</td>
<td>3.5202 \times 10(^{-9})</td>
</tr>
</tbody>
</table>

Fig. 13—Intra-particle diffusion plot for the adsorption of Cr(VI) onto STGOC

Fig. 14—Intra-particle diffusion plot for the adsorption of Cr(VI) onto CAC
Table 8. It is evident that the removal of chromium(VI) follows film diffusion process since the coefficient values are in the range of $10^{-6}$-$10^{-8}$ cm$^2$/s for both STGOC and CAC. Hence, based on Weber-Morris model and film diffusion coefficient values, it could be concluded that both film diffusion and intra-particle diffusion processes are involved in the removal of chromium(VI). Therefore, in the initial stages, sorption was due to boundary layer diffusion effect whereas, in the latter stages (linear portion of the curve), sorption was due to the intraparticle diffusion effects. 

**Desorption studies**

Desorption studies were conducted both with acid and alkali solutions. As NaOH was found to be a better desorbent, attempts were made to desorb Cr(VI) from Cr(VI) loaded STGOC and CAC using various concentrations of NaOH (0.01-1N). Results showed that about 30% and 60% of Cr(VI) could be desorbed from STGOC and CAC respectively by using 1N NaOH under optimum conditions. Similar results were reported with NaOH by studies conducted on marine algal mass. Poor desorption even with 1N NaOH show predominance of chemical bonding between STGOC and Cr(VI).

After the desorption of Cr(VI), these sorbents were washed thoroughly with distilled water. The adsorption capacities of these sorbents were again tested and three cycles of consecutive sorption-desorption operations were carried out. The values are shown in the Table 9. Results showed that the adsorption capacities of NaOH regenerated sorbents STGOC and CAC were decreasing in the range of 30-18% and 60-27%, respectively.

**Application to wastewater**

Batch experiments with chrome plating synthetic wastewater have been carried out to elucidate the adsorption capacity of these sorbents. Table 10 shows the characteristics of the synthetic wastewater used for this study and amount of Cr(VI) ions and other salts remained after adsorption. The effect of varying adsorbents dose on the removal of Cr(VI) has been carried out under optimum time and pH. Figure 15 shows the removal of Cr(VI) as a function of sorbent dose for an initial Cr(VI) concentration of 51.67 mg/L. It has been observed that for an adsorbent dose of 0.8 g/100 mL, STGOC removes a maximum of 99.36% (64.18 mg/g) Cr(VI) from wastewater where as, CAC required an adsorbent dose of 1.2 g/100 mL for the maximum removal of 98.90% (42.63 mg/g) Cr(VI) from wastewater. Hence, it is observed that STGOC is 1.5 times more efficient than CAC in the removal of Cr(VI) from wastewater.

**Characterization methods**

SEM is used to study the morphology and surface characteristics of adsorbent materials. The SEM images of STGOC, CAC and Cr(VI) loaded carbons are shown in Figs 16a, 16b, 17a and 17b, respectively. Comparing these images, it can be seen that a more uneven and rough surface morphology compared to its precursor is seen in chromium loaded carbons, which suggests that chromium ions are deposited on carbon surface. Also, density difference between chromium loaded and unloaded carbons clearly indicates that there is adsorption of chromium ions on the carbon surfaces.

<table>
<thead>
<tr>
<th>Cycle no.</th>
<th>STGOC (%)</th>
<th>CAC (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30</td>
<td>60</td>
</tr>
<tr>
<td>2</td>
<td>24</td>
<td>42</td>
</tr>
<tr>
<td>3</td>
<td>18</td>
<td>27</td>
</tr>
</tbody>
</table>

Table 9—Desorption with NaOH

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Amount before treatment (mg/L)</th>
<th>Amount after treatment (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>STGOC</td>
<td>CAC</td>
<td>STGOC CAC</td>
</tr>
<tr>
<td>Cr(VI)</td>
<td>51.67</td>
<td>0.72 1.70</td>
</tr>
<tr>
<td>Cr(III)</td>
<td>1.67</td>
<td>0.01 0.04</td>
</tr>
<tr>
<td>Sulphates</td>
<td>46.67</td>
<td>36.20 40.60</td>
</tr>
<tr>
<td>Iron</td>
<td>1.17</td>
<td>0.01 0.08</td>
</tr>
<tr>
<td>pH</td>
<td>2.00</td>
<td>2.60 3.10</td>
</tr>
</tbody>
</table>

Table 10—Removal efficiencies of adsorbents from chrome plating wastewater (synthetic)

Fig. 15—Effect of adsorbents dose on removal of Cr(VI) from chrome plating wastewater
FTIR spectroscopy was used to detect vibration frequency changes in various adsorbents before and after Cr(VI) uptake. The spectra were recorded by Shimadzu spectrometer within the range of 4000-400 cm\(^{-1}\) to identify the presence of various surface functional groups. The FTIR spectrum obtained for STGOC and CAC and Cr(VI) laden adsorbents are shown in Figs 18a, 18b, 19a and 19b. Sulphuric acid treatment introduces new functional groups such as \(-\text{SO}_3\)\(^2\)H and \(-\text{SO}_4\)\(^2\)H and as these functional groups are strong acids but their conjugates (\(-\text{SO}_3\)\(^-\) and \(-\text{SO}_4\)\(^-\)) are weak bases, these conjugates were thus considered to be able to react with metal ions relatively weakly and reversibly\(^{41}\).

A peak at 1166.85 cm\(^{-1}\) in spectra of STGOC shows the presence of \(-\text{SO}_3\)H groups and is shifted to 1145.75 cm\(^{-1}\) in the spectra of Cr(VI) loaded STGOC. The peaks at 781.12 cm\(^{-1}\) and 1033.77 cm\(^{-1}\) in the spectra of STGOC were shifted to 786.98 cm\(^{-1}\) and 1035.81 cm\(^{-1}\) respectively in Cr(VI) loaded STGOC. These peaks correspond to S=O stretching vibrations. A peak at 661.61 cm\(^{-1}\) in Cr(VI) loaded spectra is due to C-S stretching vibrations. Peaks at 1596.95 cm\(^{-1}\) and 1599.04 cm\(^{-1}\) show the presence of \(-\text{CO}\) groups. Peaks at 2912.31 cm\(^{-1}\) and 2916.47 cm\(^{-1}\) correspond to \(-\text{CH}_2\) groups.

Peaks at 1731.96 cm\(^{-1}\) and 1714.60 cm\(^{-1}\) in CAC and peaks at 1707.06 cm\(^{-1}\) and 1730.21 cm\(^{-1}\) in Cr(VI) loaded spectra may be assigned to C=O groups. Peaks at 3529.49 cm\(^{-1}\) and 3583.49 cm\(^{-1}\) in CAC show the presence of free hydroxyl groups. Peaks at 3442.70 cm\(^{-1}\) and 3479.34 cm\(^{-1}\) in the spectra of CAC and peaks at 3458.55 cm\(^{-1}\) in the spectra of Cr(VI) loaded CAC may be due to \(-\text{NH}\) stretching vibrations. Peaks at 2912.31 cm\(^{-1}\) and 2916.47 cm\(^{-1}\) correspond to \(-\text{CH}_2\) groups.
Adsorption mechanism

Based on the above results, a tentative mechanism has been proposed and is as follows:12. The presence of surface oxides, \( \text{C}_x\text{O} \) and \( \text{C}_x\text{O}_2 \) can make the carbon interact with water and cause a rise in pH due to hydrolytic reaction of water molecules, in accordance with

\[
\text{C}_x\text{O} + \text{H}_2\text{O} \leftrightarrow \text{C}_x\text{O}_2\text{H} + 2 \text{OH}^{-}
\]

\[
\text{C}_x\text{O}_2 + \text{H}_2\text{O} \leftrightarrow \text{C}_x\text{O}_2\text{H} + 2 \text{OH}^{-}
\]  

(14)

The acquisition of charge by the carbon surface then facilitates interaction with species of opposite charges. Since bichromate ions are the predominant species in solution of Cr(VI) at pH < 7.0, its removal can be expected to proceed in accordance with

\[
\text{C}_x^{2+} + \text{HCrO}_4^- \leftrightarrow \text{C}_x\text{O}_2\text{H} + \text{Cr}^3+ + 2 \text{OH}^{-}
\]

\[
\text{C}_x\text{O}_2^{2+} + \text{HCrO}_4^- \leftrightarrow \text{C}_x\text{O}_2\text{HO}_3\text{Cr}^+ + 2 \text{OH}^{-}
\]  

(15)

The combination of Eqs (14) and (15) give the overall reaction involved in the removal of Cr(VI) and may be written as

\[
\text{C}_x\text{O} + \text{H}_2\text{O} + \text{HCrO}_4^- \leftrightarrow \text{C}_x\text{O}_2\text{H} + \text{Cr}^3+ + 2 \text{OH}^{-}
\]

\[
\text{C}_x\text{O}_2 + \text{H}_2\text{O} + \text{HCrO}_4^- \leftrightarrow \text{C}_x\text{O}_2\text{HO}_3\text{Cr}^+ + 2 \text{OH}^{-}
\]  

(16)

Conclusions

The following conclusions are drawn from the present investigations:

(i) Batch studies showed that, 96.0% and 88.5% of Cr(VI) ions were removed from aqueous solution by STGOC and CAC at pH 2.5, and 1.5 and at an adsorbent dose of 0.2 g/100 mL and 0.3 g/100 mL respectively. From these results it is clear that, STGOC removes more Cr(VI) ions from aqueous solutions at a relatively higher pH, lesser contact time and with lesser adsorbent dose than that of CAC.

(ii) Langmuir and Freundlich adsorption isotherm fit well with experimental data. However, the values of correlation coefficients indicate that experimental results obtained with Freundlich isotherms are better suited than those obtained with Langmuir isotherm.

(iii) The adsorption of Cr(VI) onto these adsorbents follow pseudo-second order kinetics.

(iv) Desorption studies indicated that, by using 1N NaOH, only 30% of Cr(VI) could be desorbed from STGOC whereas 60% Cr(VI) could be obtained from chromium loaded CAC carbon. This shows a strong chemical bonding between STGOC and Cr(VI).

(v) Batch studies indicated that the performance of STGOC is 1.5 times more superior to CAC in the removal of Cr(VI) from aqueous solutions and chrome plating synthetic wastewater.

(vi) Therefore, it can be concluded from the present studies that carbon derived from GOC can be used as an alternative adsorbent for the removal of Cr(VI) from aqueous solutions and chrome plating wastewaters.
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References