Adsorption Studies on the Removal of Hexavalent Chromium (Cr (VI)) from Aqueous Solution using Black Gram Husk

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Abstract
In the current work, black gram husk (BGH) as an effective adsorbent was used to remove the hexavalent chromium (Cr (VI)) from aqueous solution in the batch mode. The characterization of adsorbent was done by Fourier transform infrared spectroscopy (FT-IR) to identify the functional groups present on the surface of BGH. The study was done with synthetic wastewater having a Cr (VI) concentration of 100 mg/L. Batch experiments were conducted to study the effects of various process parameters such as solution pH (1 – 7), adsorbent dosage (0.5 – 1.5 g/100 mL), initial Cr (VI) concentration (100 – 200 mg/L), and contact time (0 – 30 min) on the efficiency of the adsorption process. The maximum % removal of Cr (VI) was 65.23% at the optimized set of process parameters i.e. solution pH of 3, adsorbent dosage of 1 g/100 mL, contact time of 15 min. Freundlich and Langmuir adsorption isotherms were applied to investigate adsorption data. The observed experimental data fitted well to Langmuir isotherm ($R^2 = 0.9804$ and $q_{max} = 9.19$ mg/g). The reusability study showed that BGH material is recyclable up to only one cycle with 45.19% Cr (VI) removal efficiency. The obtained experimental results revealed that BGH as an efficient adsorbent may be used for the Cr (VI) removal from aqueous solutions.

Keywords: Black gram husk (BGH); Cr (VI); Adsorption; Reusability; Isotherms

1 Introduction
In recent years, the polluted water containing heavy metals has led to serious issues due to the random discharge of heavy metals in to the water bodies (1). Among the heavy metals, chromium has the harmful effects on the aquatic environment (2). Chromium occurs in two stable oxidation states i.e. trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)) in aqueous solution. Cr (VI) compounds are 500 times more toxic as compared to Cr(III) because of its high water solubility, carcinogenic, mutagenic properties (3). According to the World Health Organization (WHO), the maximum acceptable limit of hexavalent chromium concentration is 0.05 mg/L in wastewater (4). United States Environmental Protection Agency (USEPA) has recommended the acceptable level of Cr(VI) is 0.05 mg/L for potable water and is 0.1 mg/L for inland surface waters (5). If hexavalent chromium is present in water beyond the acceptable limit which causes skin irritation resulting in ulcer formation, liver damage and pulmonary congestion (6). Hence, it is necessary for industries to decrease the Cr(VI) concentration from their wastewaters to acceptable limit before discharging it into the aquatic environment. There have been various processes implemented to remove the chromium from industrial wastewater including ion exchange (7,8), electro-dialysis (9), chemical coagulation (10), nanoparticles (11), membrane filtration (12), electrochemical technologies (13), and adsorption (14, 15). These processes have many disadvantages such as high capital cost, incomplete metal removal, large quantity of toxic sludge, high energy requirement (16). However, Adsorption process has been found to be suitable process to remove toxic metals from wastewater using low cost adsorbents due to its high efficiency, simple to operate, low cost, reusability of adsorbent (17). In the recent years, many authors have utilized the various adsorbents towards the removal of chromium from wastewater such as modified groundnut hull (2), paper mill sludge (3), tea waste (5), neem leaves (18), husk of Bengal gram (19), modified corn stalks (20), fertilizer industry waste material (21), distillery sludge (22), coconut husk and palm pressed fibers (23).

To the best of our knowledge, none study has been reported in literature on the utilization of the husk of black gram for the removal of chromium from industrial wastewater. Therefore, in the present work, the possible use of the black gram husk for the removal of chromium (VI) has been investigated for the efficient removal of chromium (VI). The characterization of the BGH adsorbent was done by Fourier transform infrared spectroscopy (FTIR) analysis. Proximate analysis of the BGH was also carried out. The influence of the different process parameters like solution pH, adsorbent dosage, initial chromium (VI) concentration and contact time was studied. Reusability of the prepared adsorbent was also investigated in order to check the efficiency of BGH. Besides, the adsorption isotherms were also illustrated in the current work.

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2 Materials and methods

2.1 Materials
Potassium dichromate (K₂Cr₂O₇) was purchased from Central Drug House (P) Ltd. India. The stock solution comprising 1,000 ppm of Cr(VI) was prepared by dissolving 1.4134 g of K₂Cr₂O₇ in 500 ml of distilled water. All desired concentrations were prepared by appropriately diluting of the stock solution. 0.1 M NaOH and 0.1 M H₂SO₄ were used to adjust the required pH of solution before starting the experiments. Distilled water was used throughout all the experiments.

2.2 Preparation of adsorbent
Black gram (Vigna Mungo) Husk (BGH) was collected from flour mill located at Gajraula, UP, India. Initially, the BGH was washed thoroughly in running tap water followed by distilled water to remove color and dirt particles. It was then dried in oven at 110°C for 2 h. After drying, BGH was crushed in mixer grinder to make fine powder and sieved through a 25 mesh sieve tray. Synthesized adsorbent was kept in air-tight polythene bag for future use. Flow diagram for the presentation of the absorbent is shown in Figure 1. The proximate analysis of the adsorbent was carried out and the obtained results are shown in Table 1.

2.3 Characterization of BGH
The BGH adsorbent was characterized using FTIR spectra. To check the presence of functional groups in BGH, Fourier-transform infrared spectroscopy (FTIR) of the adsorbent was done by infrared spectrophotometer (model: 8400S, Shimadzu) ranging from 400 cm⁻¹ to 4000 cm⁻¹.

2.4 Batch adsorption studies
The adsorption of Cr (VI) from aqueous solution was carried out in a batch system. The experiments were conducted with 100 mL solutions of 100 ppm Cr (VI) concentration in 250 mL glass flasks at the temperature of 25°C. The batch adsorption experiments were studied to check the effect of major process parameters such as solution pH, adsorbent dosage and initial Cr(VI) concentration on the removal efficiency of Cr (VI). The mixture was stirred at 150 rpm for a fixed period of time. The adsorbent laden Cr (VI) was separated by Whatman filter paper and the clear solution was analyzed for Cr (VI) concentration. Experimental set-up with range of process parameters is shown in Fig.2. To optimize the pH value, the effect of solution pH on the removal of Cr (VI) was investigated over a pH range of 1.0–7.0. The effect of adsorbent dosages from 0.5 to 1.5 g/100mL was carried out. Effect of initial Cr (VI) concentration was studied by varying the concentration of Cr (VI) from 100 to 200 mg/L. Adsorption isotherm was studied with different initial concentrations of Cr(VI) from 100 to 200 mg/L at the constant adsorbent dosage of 1g/100 mL, temperature of 25°C and pH of 3. The observed results were analyzed by two isotherm models such as Freundlich and Langmuir.

2.5 Analytical procedure
The remaining concentration of Cr(VI) in the solution after experiments was determined by UV–visible spectrophotometer (JASCO, V-530) at 540 nm. Solution pH was determined by digital pH meter. Reproducibility of experimental results was examined by performing the experiments at least two times to obtain an average value and the experimental errors were found to be within ± 4%. The percentage removal efficiency of Cr (VI) was determined by following Eq. (1).

\[
\% \text{ Removal of Cr (VI)} = \frac{C_0 - C_e}{C_0} \times 100
\]

Figure 1: Flow diagram for the preparation of adsorbent
Adsorption capacity \( (q_e) \) was determined using following Eq. (2).

\[
q_e = \frac{C_0 - C_e}{M} \times V
\]

where, \( V \) is volume of the solution in L and \( M \) is the mass of the adsorbent used in g.

Table 1: Proximate analysis of adsorbent (BGH)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value (%)</th>
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<tbody>
<tr>
<td>Moisture Content</td>
<td>6.80</td>
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<tr>
<td>Volatile matter</td>
<td>70.80</td>
</tr>
<tr>
<td>Ash content</td>
<td>14.10</td>
</tr>
<tr>
<td>Fixed Carbon</td>
<td>8.30</td>
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</table>

3 Results and Discussions

3.1 FTIR analysis

In the present study, the FTIR spectrum was obtained to identify the functional groups present on the surface of prepared adsorbent. FTIR spectrum of the adsorbent (Shown in Fig. 3) was measured within the range of 500-4000 cm\(^{-1}\) wave number. FTIR study indicated that functional groups like C=O, C–O, O–H and N–H were present onto the BGH surface. The observed peak at 3745.50 and 3407.98 cm\(^{-1}\) is assigned due to the presence of O–H groups on the surface of BGH. A characteristic peak at around 3339.51 cm\(^{-1}\) may be due to the N–H symmetric stretching vibration indicating the presence of amino (-NH\(_2\)) groups (16). The presence of peaks observed at 2899.78 cm\(^{-1}\), 2888.20 cm\(^{-1}\) and 2833.24 cm\(^{-1}\) may be due to the stretching vibration of the –C–H group (5). The band 2363.60 cm\(^{-1}\) is the result of stretching vibrations of C=O or N–H groups possibly due to amines and ketones (24). The peak at around 1632.63 cm\(^{-1}\) may be due to the stretching vibration of amide groups. The absorption band near 1520.77 cm\(^{-1}\) may be assigned to the –C–H deformation vibration indicating the presence of alkanes group. The characteristics peak at 1397.33 cm\(^{-1}\) was due to the stretching vibration of –C–O. The peak observed at 1326.93 cm\(^{-1}\) and 1088.74 cm\(^{-1}\) may be assigned to the C–OH stretching vibration of carboxylic acid and alcohols (5, 24). The absorption band between 600 and 900 cm\(^{-1}\) comprises several bands associated to the aromatic and out of plane –C–H bending (5, 25).
3.2 Optimization of Solution pH

The solution pH is an important parameter in deciding the removal efficiency of Cr (VI). To find the optimum pH, experiments were conducted over a various range of pH values from 1.0 to 7.0. Fig. 4 depicts the removal efficiency of Cr (VI) versus solution pH. Figure 4 shows that the % removal of Cr(VI) was increased from 42.14 to 65.23% for an increase in solution pH from 1 to 3. Then, the percentage removal was reduced to 19.32% with more increase in the pH up to 7.0. The obtained results showed that the maximum 65.23% of Cr(VI) by the prepared adsorbent (BGH) was removed at the optimized pH of 3.0. Hence, the optimum pH was selected as 3.0 to achieve the suitable removal efficiency of Cr(VI) for all the remaining experiments.

Hexavalent chromium (Cr(VI)) may occur in the aqueous medium in various anionic forms i.e. chromate (CrO$_4^{2-}$), dichromate (Cr$_2$O$_7^{2-}$), or hydrogen chromate (HCrO$_4^{-}$) as per the following Eq. (3):

$$2H^+ + 2HCrO_4^- \leftrightarrow 2H_2CrO_4 \leftrightarrow 2H_2O + CrO_2^{7-} \leftrightarrow 2CrO_3^- + H_2O$$

It is well reported in literature that the dominant form of Cr(VI) at lower pH is HCrO$_4^{-}$ (5). When the solution pH increases, the concentration of HCrO$_4^{-}$ is shifted to other forms such as CrO$_2$ 4− and Cr$_2$O$_7^{2-}$. It can be established that the active form of Cr(VI) is HCrO$_4^{-}$ that can be adsorbed by the BGH in this work.

3.3 Effect of Adsorbent dosage

The effect of adsorbent dosage was investigated by varying the amount of adsorbent from 0.5 to 1 g/100 mL. The obtained results of adsorbent dosage on the % removal of Cr (VI) are depicted in the Fig. 5. It can be seen from figure 5, the adsorption of Cr (VI) increases with an increase in adsorbent dosage due to an increase in the number of adsorption sites and enhance surface area (22). Number of adsorption sites available for the adsorption of Cr (VI) is directly proportional to surface area of the adsorbent (5). It was further observed that the increasing amount of BGH had no noticeable effect on the removal efficiency of Cr(VI).

3.4 Effect of initial Cr(VI) concentration

The effect of initial Cr(VI) concentration on the removal efficiency was studied under the optimum conditions i.e. solution pH of 3, time of 15 min, temperature of 25°C and...
adsorbent dosage of 1 g/100 mL. The initial Cr (VI) concentration was varied from 100 to 200 mg/L. The observed results are shown in Fig.6.

![Figure 5: Effect of adsorbent dosage on the removal efficiency of Cr (VI).](image)

Figure 5: Effect of adsorbent dosage on the removal efficiency of Cr (VI) (Experimental conditions: Solution pH = 3; T = 25°C; Time = 15 min; Initial Cr (VI) concentration = 100 mg/L; Solution volume = 100 mL)

It was observed that percentage removal of Cr(VI) was decreased from 65.23% to 41.25% when the initial Cr(VI) concentration increased from 100 to 200 mg/L. This may be attributed to enhance in the number of chromium ions for a fixed dosage of the adsorbent, the total available adsorption sites were restricted and therefore decreasing trend in % removal of Cr (VI) (2, 5). The observed results are consistent with the previous studies reported showing that the Cr (VI) removal efficiency using adsorption is inversely proportional to the initial concentration of Cr (VI) (2, 20-21).

![Figure 6: Effect of initial Cr (VI) concentration on the removal efficiency of Cr (VI).](image)

Figure 6: Effect of initial Cr (VI) concentration on the removal efficiency of Cr (VI) (Experimental conditions: Adsorbent dosage = 1 g/100 mL; Solution pH = 3; T = 25°C; Time = 15 min; Solution volume = 100 mL)

3.5 Effect of contact time

The experiments were conducted at the optimized conditions such as adsorbent dosage of 1 g/100 mL, pH of 3, initial Cr (VI) concentration of 100 mg/L and temperature of 25°C. It was observed that percentage removal of Cr (VI) was improved from 29.54 to 65.23% in initial 15 min after that no removal in chromium was seen. This is mainly because of the fact that all the available adsorbing sites on the adsorbent surface are engaged and no further adsorption is possible (5). Therefore, time was selected as 15 min for all the experiments in the present study.

3.6 Adsorption Isotherms

In order to optimize the design of an adsorption method, it is necessary to create the most suitable correlation for the equilibrium curve. Several isotherms are available for analyzing experimental data but in this study the obtained equilibrium adsorption data were fitted to the Freundlich and Langmuir as following.

3.6.1 Freundlich isotherm

The linear form of Freundlich isotherm can be represented by Eq. (4):

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$

where, $q_e$ is equilibrium concentration (mg/L), $K_f$ is the Freundlich isotherm constant (L/mg) and $n$ is the Freundlich adsorption intensity. Freundlich isotherm model has been plotted between log $q_e$ against log $C_e$ (shown in Fig. 8 (a)).

![Figure 7: Effect of contact time on the removal efficiency of Cr (VI).](image)

Figure 7: Effect of contact time on the removal efficiency of Cr (VI) (Experimental conditions: Adsorbent dosage = 1 g/100 mL; Solution pH = 3; T = 25°C; Initial Cr (VI) concentration = 100 mg/L; Solution volume = 100 mL)

3.6.2 Langmuir isotherm

The linear form of Langmuir isotherm model is given by the following Eq. (5):

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{K_Lq_{max}}$$

where, $q_e$ is the amount of the adsorbate adsorbed (mg/g) at equilibrium, $q_{max}$ is the maximum monolayer adsorption capacity (mg/g) and $K_L$ is the Langmuir isotherm constant (L/mg) that is associated to adsorption energy. Langmuir plot of $C_e/q_e$ vs $C_e$ is depicted in Fig. 8(b). The values of Langmuir parameters $K_L$ and $q_{max}$ were determined using the intercept and slope. The isotherm parameters and correlation coefficient ($R^2$) are presented in Table 2. The value of Freundlich constant ($n$) was greater than 1 indicating a strong interaction between BGH and Cr (VI). Amongst the correlation coefficient obtained from different two isotherms, Langmuir isotherm model provided the best fitted data for the adsorption of Cr (VI) giving the higher value of regression coefficient ($R^2 = 0.9804$).

3.7 Reusability of the prepared adsorbent

Reusability of the any prepared new material is the most notable advantage for the treatment of wastewater. Hence, a reusability test of the adsorbent was conducted at the optimized conditions (Initial Cr (VI) concentration = 100 mg/L; pH = 3.0; Temperature = 25°C; Contact Time = 15 min, adsorbent dosage = 1 g/100 mL) where the maximum removal efficacy was achieved. In the present work, reusability of the used material was examined by regenerating the adsorbent laden with Cr (VI) using the method reported in literature (26). The regeneration study for Cr (VI) adsorption was carried out using 1 M HCl and found that the removal efficiency of Cr(VI) was reduced from
65.23% to 45.19% after one cycle. Almost 31% reduction in the efficiency of Cr (VI) removal was obtained after one cycle.

![Graph of Freundlich and Langmuir isotherms for Cr (VI) adsorption on BGH](image)

Figure 8: (a) Freundlich isotherm (b) Langmuir isotherm for the Cr (VI) adsorption on BGH (Experimental conditions: Adsorbent dosage = 1 g/100 mL; Solution pH = 3; T = 25°C; Time = 15 min; Solution volume = 100 mL)

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<th>Isotherm model</th>
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<td>Freundlich</td>
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<tr>
<td></td>
<td>R²</td>
<td>0.61</td>
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<tr>
<td></td>
<td>q_n (mg/g)</td>
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<tr>
<td>Langmuir</td>
<td>q_max (mg/g)</td>
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<tr>
<td></td>
<td>R²</td>
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</tr>
<tr>
<td></td>
<td>K_L (L/mg)</td>
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</tr>
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</table>

Table 2: Freundlich and Langmuir isotherm parameters for the adsorption of Cr (VI) onto BGH

4 Conclusion

The present study has shown the efficiency of BGH as an effective adsorbent for the removal of Cr(VI) from aqueous solution. The effect of solution pH, adsorbent dosage, initial Cr (VI) concentration and contact time were examined in order to optimize the process conditions for the maximum removal of Cr(VI). Maximum 65.23% of Cr (VI) was removed from wastewater at the optimum conditions i.e. pH of 3, adsorbent dosage of 1 g/100 mL, initial Cr (VI) concentration of 100 mg/L and contact time of 15 min. It was observed that adsorption using BGH was very much dependent on the solution pH. Langmuir isotherm was found to be well fitted with a high correlation coefficient (R² = 0.9804) as compared to Freundlich isotherm with a correlation coefficient (R² = 0.6168). Moreover, the monolayer maximum adsorption capacity (q_max) was found to be 9.19 mg/g. The reusability test of the BGH revealed that the % removal of Cr (VI) was reduced from 65.23% to 45.19% after one cycle. The obtained results from the present work, the BGH is an effective adsorbent and may be utilized efficiently in the removal of Cr (VI) from aqueous solutions for the purposes of environmental cleaning.

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Ethical issue

Authors are aware of, and comply with, best practice in publication ethics specifically with regard to authorship (avoidance of guest authorship), dual submission, manipulation of figures, competing interests and compliance with policies on research ethics. Authors adhere to publication requirements that submitted work is original and has not been published elsewhere in any language.

Competing interests

The authors declare that there is no conflict of interest that would prejudice the impartiality of this scientific work.

Authors’ contribution

All authors of this study have a complete contribution for data collection, data analyses and manuscript writing.

References


