Rational suitability of low cost activated carbon in removing hexavalent chromium ions from wastewater by uninterrupted mode of adsorption

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Abstract. Heavy metals such as chromium, lead, arsenic and others are dense metals whose contamination of water may exterminate life on earth at the niche in industrial activities, foodstuffs or medicines and so on. Activated carbons are very helpful in removing heavy metal ions from aqueous solutions by adsorption, and have been investigated by many researchers so far. The practical relevance of activated carbon made from de oiled soya in the removal of hexavalent chromium ions through continuous adsorption mode is reported in this paper. A breakthrough plot was plotted in finding the effect of initial concentration and adsorbent bed height in the adsorption of hexavalent chromium through activated carbon of de oiled soya. The breakthrough time and saturation time increased as the concentration of the initial solution shot up from 40 mg/L to 60 mg/L. The saturation time was in an incremental mode when the thickness of the adsorbent bed height in a fixed bed was increased from 5cm to 7cm for 40 mg/L initial concentration of hexavalent chromium. The Adams-Bohart’s model was found to fit perfectly the fixed bed column in the removal of hexavalent chromium from aqueous solutions. The fabricated adsorbent worked well in detoxifying hexavalent chromium metal ion contaminated wastewater.

Key words: Activated carbon, breakthrough curve, De oiled soya, fixed bed column, heavy metal.

1. Introduction
Elements that are metallic in nature and having more density than that of water are said to be heavy metals. Numerous industrial segments stipulate the usage of heavy metals to a great extent. Despite advancement in pollution management techniques, heavy metals reach the environment mainly through wastewater discharge. Toxic metals like chromium, lead, copper, cadmium, etc., even at low levels of exposure provoke toxicity [1]. Many heavy metals such as chromium are essential for physiological functions in a living being. However, a surplus amount of these metals are unfavorable to humans and impact health. Heavy metal such as chromium, (there is not much worth in mentioning variations in the concentrations between favorable and unfavorable effects) is toxic [4,5]. Chromium is very toxic when inhaled or enters the body through skin as it causes lung cancer, nasal irritation, nasal ulcer, etc. The Environmental Protection Agency (EPA) has specified standards for water which should contain 0.1 milligrams per liter (mg/l) of chromium ion [6]. Chromium affects...
various components of the immune system and can result in immunostimulation. Exposure to hexavalent chromium (Cr(VI)) can also result in various point mutations in DNA, and lead to chromosomal damage, as well as oxidative changes in proteins [7]. Treatment of wastewater containing heavy metals can be accomplished by several techniques such as precipitation[8], evaporation, adsorption, etc. Among the available techniques, adsorption using activated carbon as an adsorbent sounds effective [9]. Actual applications of such adsorption systems involve the use of continuous sorption columns.

The objective of this work aimed to evaluate the performance of the activated carbon fabricated from De oiled soya in the removal of hexavalent chromium(Cr(VI)) ion through fixed bed column adsorption which sounds good in practical application of adsorption process. Activated carbon of de oiled soya was abbreviated as DOSAC throughout this article. Batch adsorption studies were conducted to optimize the process parameters such as solution pH, DOSAC dose, contact time and initial Cr(VI) ion concentration. The vibrant conduct of fixed-bed (continuous adsorption)column was described using breakthrough curve. Effects of initial Cr(VI) ion concentration and effects of bed height on the ratification of Cr(VI) ion adsorption was illustrated in the present study.

2. Materials and Methodology
De oiled soya is a derivative of a bean called Glycine Max, commonly known as soybean. It is a legume plant native to East Asia and widely grown for its bean which is edible in nature. Soya oil is prepared by crushing the soya bean and the waste product, after the extraction of the oil is called de oiled soya. De oiled soya was collected from a private industry in Tamilnadu.

2.1. DOSAC preparation
The production of DOSAC that incorporated in this segment was explained in authors’ own article [10]. Carbon that was produced through a 150 µ sieve and hung in a 90 µ sieve was kept in an airtight container. DOSAC [10] is shown in Figure1.

![Figure 1. Activated carbon of de oiled soya](image)

2.2. Batch adsorption studies
Intermittent adsorption studies namely batch experimental studies were undertaken to find out the effect of process parameters on adsorption capacity of DOSAC. The process parameters such as solution pH, DOSAC dose, contact time and Cr(VI) ion concentration. Table 1 explained about the lower and upper limits of the chosen process variables in the conduct of the batch adsorption studies.
The effect of the process parameters had been assessed by conducting the batch experimentation by incorporating the variation in each parameter as shown in the table.

**Table 1. Batch adsorption experimentation process parameters**

| Process parameter   | Lower limit | Upper limit | Interval |
|---------------------|-------------|-------------|----------|
| pH                  | 2           | 10          | 1        |
| DOSAC dose          | 0.1 g       | 0.4 g       | 0.05 g   |
| contact time        | 20 min      | 160 min     | 20 min   |
| Cr(VI) ion concentration | 10 mg/L     | 80 mg/L     | 10 mg/L  |

The following observations were obtained from batch adsorption studies:

- the adsorption capacity was increased on decreasing the pH of the Cr(VI) ion solution
- adsorption of Cr(VI) ion was increased by increasing the DOSAC dose
- additional amplification in contact time did not show any implication on adsorption of Cr(VI) ion
- an increase in adsorption was reflected due to the decrease in the initial concentration of Cr(VI)

Based on the observations made in batch adsorption studies the limits were set for column adsorption experimentation.

2.3. Uninterrupted(Continuous) flow mode or column adsorption mechanism

The efficacy of an adsorbent in removing any pollutant from wastewater is done by the column adsorption procedure. A fixed bed column of 1.75 cm diameter and 50 cm height was fabricated in glass. It had an aperture at the base which could be turned by a valve. The column was packed by DOSAC for a requisite depth over a layer of 1 cm glass wool which was placed near the column’s opening to keep the adsorbent in a firm position. Figure 2 shows the setup for the column experimentation.

![Figure 2. Graphical exhibit of the fixed bed column setup](image)

Uniform packing was facilitated with a glass rod by tapping and tamping the adsorbent. Further, this setup was kept in sunlight for 3 days for the packed carbon to be completely dry. Fixed concentration of synthetic Cr (VI) solution was filled in the column. The Cr (VI) solution was made to
enter the column at a preset flow rate (2.5 ml / min). After a specific time frame, the resultant solutions were gathered and examined spectrometrically. The impact of Cr (VI) ion concentration and DOSAC bed height were investigated for various combinations. Table 2 shows the various combinations of input variables for the adsorption process.

Table 2. Combinations of input variables for the column adsorption process

| Name of the variable            | Upper limit | Lower limit |
|---------------------------------|-------------|-------------|
| Initial concentration of Cr(VI) ion | 40 mg/L     | 60 mg/L     |
| Bed height of DOSAC             | 5 cm        | 7 cm        |

Breakthrough time and its curve profile determine the competence of the adsorption column. Adams-Bohart’s model was related to the column’s statistics to exemplify the first portion of breakthrough curve. The unique parameters of column testing using Adams–Bohart’s model establishes the basic equation describing the association between ln (Ct/C0) and contact time ‘t’ in continuous adsorption mode. This methodology highlights the estimation of parameters such as maximum adsorption capacity (No) and kinetic constant (kAB). The results obtained in the fixed bed column experimentation were imposed on Adams-Bohart’s equation. The Adams–Bohart’s equation is

\[
\ln \frac{C_t}{C_0} = -k_{AB} C_0 t + k_{AB} N_o Z / U_o
\]

where \(C_t\) is the equilibrium metal ion concentration (mg/L), \(k_{AB}\) the Adams-Bohart’s kinetic constant in L/mg min, \(N_o\) and \(Z\) are the adsorption capacity per unit volume of the adsorbent (saturation concentration in mg/L) and bed depth of the column (cm) correspondingly. \(U_o\) denotes linear velocity (cm/min). The values of \(k_{AB}\) and \(N_o\) were acquired from the plot of ln \((C_t/C_0)\) versus time t.

3. Discussions on outcomes obtained

3.1. Characterization of DOSAC

DOSAC underwent a characterization study through a Scanning Electron Microscope (SEM) analysis. The study showed that DOSAC had potential pores to remove Cr (VI) ion from synthetic solution by fixing the pollutant to its pores as shown in figure 3.

![Figure 3. SEM photograph of DOSAC](image)
3.2. Continuous adsorption study (Fixed bed column study)

Column adsorption was carried with the designed column at a stable flow rate of 2 ml/min. A breakthrough graph was plotted between contact time in X axis and $C_t / C_0$ in the Y axis. Adsorption information was applied to the segment hypothesis to get measurements of the impact boundaries.

3.2.1. Impact of Initial Concentration of Chromium[Cr(VI)] solution

The adsorption process was conducted at different initial concentrations of 40 and 60 mg/L by maintaining the bed height $Z$ as 5 cm. Breakthrough curve is exhibited in figure 4. The breakthrough curve was linear as at the initial stage, the equilibrium concentration was almost zero. The rationale behind it is that at the primary stage the column bed completely adsorbed all metal ions and with the passage of time the bed became worn out and hence did not adsorb matter from the solution. It is found from Figure 4, that unadsorbed metal ion concentration was improved by increasing the initial concentration of the Cr (VI) ion. The influential dynamism of adsorption is the focus on the difference between the solute in the adsorbent and the solution. This proved that the adsorbent bed was saturated quickly with a superior amount of initial concentration [12]

For 40 mg/L concentration of Cr(VI) ion adsorption as shown in Figure 4, the breakthrough time of adsorption was 420 min and saturation of the bed was reached at 1320 min. Breakthrough time was reached at 400 min for initial concentration of 60 mg/L Cr (VI) ion and the corresponding saturation point was attained at 1140 min.

![Figure 4. Breakthrough plot of the impact of initial concentration for adsorption of Cr (VI) ion (bed height $Z = 5$ cm)](image)

3.2.2. Impact of bed height on adsorption

Optimum performance of the continuous fixed bed column adsorption with respect to bed height was inculcated in the bed height of 5 and 7 cm. The input solution’s concentration was 40 mg /L and a velocity of 2 ml/min was kept constant. From figure 5, it can be understood that as the bed height increased, both saturation time and breakthrough time were also extended [13] which was due to more number of adsorbent particles being available for the adsorbate. It was found that the breakthrough time was attained at 420 minutes for a 5 cm bed height and 480 minutes for a bed height of 7 cm.
3.2.3 Adams-Bohart’s model for fixed bed column
The preliminary part of the adsorption was predicted by the Adams-Bohart’s model. Equation 2 is the Adams-Bohart’s column model representation.

\[
\ln \frac{C_t}{C_0} = -k_{AB} C_0 t + \frac{k_{AB} N_o Z}{U_o}
\]  

(2)

Adams-Bohart constants were derived from the graph (Figure 6) drawn between the values of \(\ln(C_t/C_0)\) versus time, where \(C_t\) is the outlet metal ion concentration (mg/L), \(k_{AB}\) (L/mg min) is the Adams-Bohart’s kinetic constant, \(N_o\) (mg/L) and \(Z\) (cm) are the adsorption capacity per unit volume of the adsorbent column and the bed depth of the column respectively. Adams-Bohart’s model column adsorption of Cr (VI) adsorption is displayed in Figure 6.

![Figure 6. Adams-Bohart’s model](image-url)
Analysis and results of the Adams-Bohart’s constants for fixed bed column are shown in Table 3 which revealed that as the initial concentration of the solute increased, $N_0$ [14] increased whereas, $K_{AB}$ decreased. As bed height increased from 5 cm to 7 cm $N_0$ decreased while $K_{AB}$ increased [14]. The parameters applied in this study depicted the influence on the breakthrough for metal ion.

Table 3. Adam-Bohart’s parameters at different conditions for the adsorption Cr(VI) of the fixed bed column

| Concentration of Cr(VI) ion(mg/L) | Bed height (cm) | $K_{AB}$ (L/mg min) | $N_0$(mg/L) | Breakthrough Time(min) | Saturation time(min) |
|----------------------------------|----------------|----------------------|-------------|------------------------|----------------------|
| 40                               | 5              | 0.000050             | 2169.66     | 420                    | 1320                 |
| 60                               | 5              | 0.000033             | 3199.09     | 400                    | 1140                 |
| 40                               | 7              | 0.000050             | 1668.01     | 480                    | 1500                 |

From Table 3, it is seen that any alteration in the bed height of the adsorbent significantly affected the performance of the fixed bed column by losing the speed of exhaustion time. However, the alteration particularly increased in the initial concentration of metal ion in aqueous solution as it speeded up exhaustion of the adsorbent bed.

4. Concluding Remarks

It can be concluded that DOSAC that is the activated carbon of de oiled soya, is appropriate for removal of hexavalent chromium (Cr (VI)) ions from an aqueous solution. The breakthrough plot depicted that as the initial concentration and influence of bed height increased, adsorption of Cr (VI) ion also increased. Breakthrough time and saturation time were 420 minutes and 1320 minutes for 40 mg/L initial concentration at 5 cm bed height. Breakthrough time and the saturation time were 400 minutes and 1140 minutes for 60 mg/L initial concentration at 5 cm bed height. Breakthrough time and saturation time were 480 minutes and 1500 minutes for 40 mg/L initial concentration at 7 cm bed height. Both breakthrough time and saturation time were reduced as the initial concentration increased. The perfect fit of the Adams-Bohart’s model through the fixed bed column revealed that the removal of Cr (VI) ions from aqueous solution using DOSAC was good enough to use activated carbon on a large scale to detoxify metal-contaminated wastewater.

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