

# Fabrication and Application of Cost-effective Activated Carbons in Removing Hexavalent Chromium Metal – Newfangled Material in Detoxification Perspective

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## Abstract

As the need for the hour is to promote healthy environment for the betterment of mankind to survive, this research progressed in removing the heavy metals from the wastewater through a simple technique known as adsorption. The elimination of chromium ions from wastewater by exhausting two types of activated carbon made from waste material de-oiled soya and *Manilkara zapota* tree wood was explored. The effect of adsorption variables namely pH, adsorbent dose, initial concentration of hexavalent chromium, and contact time were analyzed. High initial concentration showed better results in metal adsorption. The adsorption isotherm models Langmuir and Freundlich agreed well with the adsorption studies of both activated carbons, with correlation co-efficient approaching. The kinetic analysis found that pseudo-second order kinetics accurately predicted experimental data with a correlation value of 0.998. Among the two activated carbons, the activated carbon of *M. zapota* showed slightly better performance than in removing the hexavalent chromium with a maximum uptake of 27.778 mg/L. The findings indicate that activated carbons may be employed as a worthwhile adsorbent for removing hexavalent chromium ion to convert more harmful wastewater to less harmful wastewater.

## Keywords

Adsorption capacity, Metal toxicity, Isotherm, Kinetics

## Introduction

Elements of atomic numbers more than 20 are termed as heavy metals. Zinc, cadmium, chromium, copper, mercury, and lead are the prevalent heavy metal contaminants. When heavy metals are unabsorbed by physiological activities, and they start accumulating in soft tissue that become poisonous in due course of time toxicity is determined by solubility. The toxicity of insoluble substances, as well as metallic versions, is frequently insignificant. The element chromium is a micronutrient. Hexavalent chromium is a pollutant that is both poisonous and mutagenic. The presence of an excessive quantity of metal, especially heavier one, is a contaminant in making the water unfit. Several studies and interpretations have shown that with larger concentrations of heavy metal, many living things' organs can be harmed, resulting in catastrophic illnesses. Many health issues, such as chromosomal damage [1], acute tubular necrosis, mouth ulcers, vomiting, stomach discomfort, renal failure, and mortality have been reported [2, 3]. Food and water are both sources of hazardous substances that enter the human body. Because of industrial usage, unregulated coal burning, and natural disasters,

mankind is now exposed to the greatest levels in recorded history. Individuals are more prospective to be wide-open to chromium poisoning while drinking water, and those harmful metals bioaccumulate in the human body as a result. Many studies have found that chromium levels in drinking water are greater than the World Health Organization acceptable limit (0.05 mg/L) [4, 5].

### An eye on techniques to expel hexavalent chromium toxic metals from aqueous solution

As of now fit water is a rudimentary need for life and every researcher aims at removing such toxic chromium from aqueous solution by traditional treatment methods that largely categorized into physical, chemical, and biological [6]. For treating wastewater, several procedures for instance coagulation, precipitation, oxidation, ion exchange, and membrane filtering were used [7, 8]. The biggest downside of the above-mentioned procedures, however, was the treatment duration and cost. The costs of these treatment procedures are quite costly, and the industries' income has suffered as a result. To address these issues, a technology known as activated carbon adsorption was created [9]. Adsorption methods which have been proved to be better technique in detoxifying the chromium polluted water [10] but the need for the hour for the researcher to emerge with a new adsorbent which is a substance that is engaged in adsorbing the heavy metals (adsorbate) from wastewater. In this context two adsorbents in the form of activated carbon were prepared by the researcher in elimination of chromium toxicity. One is from the *M. zapota*, and another is from de oiled soya. Batch equilibrium experimentation was conducted individually, and results were compared. To check the efficiency of the batch adsorption process, adsorption isotherms and kinetic models were applied on batch adsorption data.

### Removal of hexavalent chromium by nanoparticles

Hexavalent chromium, often denoted as Cr(VI), is a toxic and carcinogenic form of chromium commonly found in industrial effluents, making its removal from water sources a significant environmental concern. Nanoparticles have shown promise in efficiently adsorbing and removing hexavalent chromium due to their high surface area, reactivity, and tunable properties. The content below depicts some ways nanoparticles can be employed for the removal of hexavalent chromium.

Nanoparticles possess high surface areas and reactive sites. These properties make them effective adsorbents for hexavalent chromium in adsorption technique. Modifying the surface of nanoparticles with specific functional groups can enhance their affinity for hexavalent chromium ions, improving the adsorption capacity. For example, functionalizing carbon-based nanoparticles with amino or hydroxyl groups can enhance chromium adsorption. Creating nanocomposites by combining nanoparticles with other materials (e.g., polymers, clays) can enhance the overall removal efficiency. Magnetic nanoparticles, such as magnetite ( $\text{Fe}_3\text{O}_4$ ), can be easily separated from water using an external magnetic field after adsorption. This makes the removal process more convenient and allows for the recovery and reuse of the nanoparticles. Nanoparticles embedded [11] in polymeric matrices can

provide a stable and controlled environment for hexavalent chromium removal. Additionally, factors such as cost, scalability, and environmental impact should be considered when designing practical applications for water treatment.

## Materials and Method

De-oiled soya and *M. zapota* tree wood was converted into activated carbon [12]. These adsorbents were subjected to the characterization study to get to know their properties in removing the hexavalent chromium from wastewater. Characterization study for instance scanning electron microscopy and Fourier transform infrared spectroscopy were executed. In addition to it X-ray diffraction, elemental analysis, and X-ray fluorescence examination were also executed and all results were published by Sujatha and Sivarethinamohan [12]. From this article it was well known that both the adsorbents were satisfactorily possessed good adsorption properties which could well suit to adsorb heavy metals such as hexavalent chromium. With that article as a base this research was conducted to determine the efficiency of these activated carbons. The batch adsorption experimentation will be influenced by many independent variables. This study considered the independent variables such as adsorbent dosages, pH, contact time, and metal ion concentration. With a batch experimental setting, the overall impact of those chosen variables on the adsorption capacity of the adsorbent was observed. To check the suitability of the adsorption isotherms like Freundlich and Langmuir models were applied. Pseudo kinetic models pertinent to the first kinetics were also analyzed on adsorption process. Table 1 portrayed the variations applied in the adsorption process variables.

Adsorption process variables	Lower limit	Interval	Upper limit
pH	2	1	10
Adsorbent dosage (g)	0.1	0.05	0.4
Contact time (min)	20	20	160
Concentration of hexavalent chromium metal ion (mg/L)	10	10	80

## Results and Discussion

### Influence of pH on hexavalent chromium adsorption

The influence of acidity in the adsorption process was done by altering the pH of the adsorbate from 2 to 10 at room temperature. The graph was plotted (Figure 1) with pH in X-axis, percentage removal of hexavalent chromium in primary Y-axis and the adsorbents adsorption capacity in the secondary Y-axis. From figure 1 was inferred that the percentage removal of hexavalent chromium and the adsorption capacity were increased on decreasing the pH of the solution [13]. At pH 4, maximum percentage removal of hexavalent chromium of 83.12% was obtained by activated carbon of *M. zapota* with adsorption capacity 16.624 mg/g. Adsorption process reached equilibrium at pH 3 with 82.12% removal of hexavalent chromium ion and with 16.124 mg/g of adsorption capacity with activated carbon of de-oiled soya. In both the cases of adsorbents, the uptake of hexavalent chromium was maximized at low pH (4 and 3) [14]. The

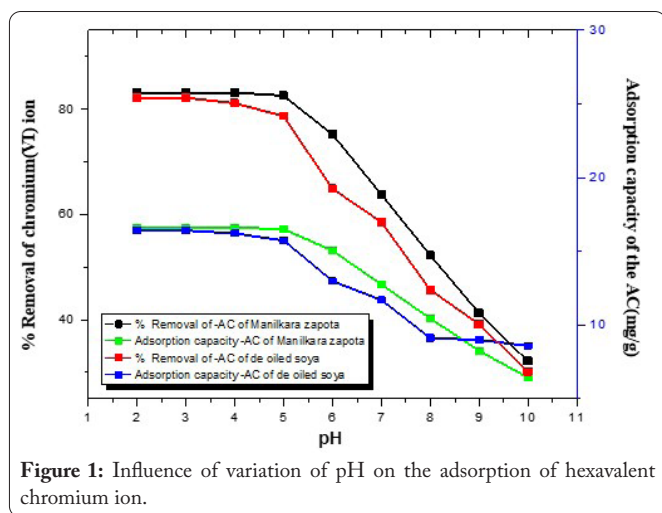


Figure 1: Influence of variation of pH on the adsorption of hexavalent chromium ion.

low pH value indicates that the neutralization of negative charges occurs at the surface of the adsorbent [15] leading to more active surface of the adsorbent. Reduced adsorption of hexavalent chromium at pH standards larger than six owing to the double competition of anions ( $\text{CrO}_4^{2-}$  and  $\text{OH}^-$ ) that were populated on the exterior of the activated carbon than chromium ions [16].

### Adsorption of hexavalent chromium with different adsorbent doses

The adsorbent dose was altered from 0.1 to 0.4 g with 0.05 g increment, to study the variation in the adsorption against the different doses. Results were graphically represented in figure 2. Figure 2 gave the deduction that adsorption of hexavalent chromium ion was augmented by increasing the adsorbent dose [17]. The escalation in percentage removal of hexavalent chromium with escalation in adsorbent quantity owe to the more accessibility of the sites. The maximum removal was witnessed with adsorbent dose as about 0.2 g of activated carbon of *M. zapota* and 0.25 g of activated carbon of de-oiled soya. Any subsequent increase in dosage had no effect on the adsorption yield, which might be owing to particle overpopulation. As a result, the ions destined to the adsorbent and the amount unadsorbed ions remain persistent even when the adsorbent dose is increased.

The percentage removal at optimum dose was 83.12% and 87.11% for activated carbon of de-oiled soya and *M.*

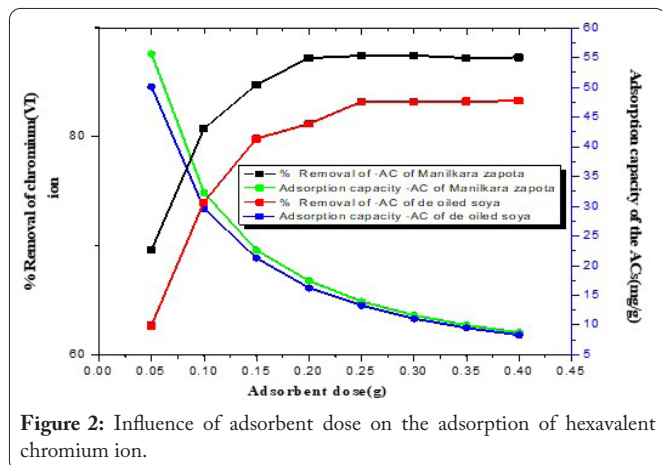


Figure 2: Influence of adsorbent dose on the adsorption of hexavalent chromium ion.

*zapota*, respectively, and 17.422 mg/g and 13.992 mg/g were corresponding adsorption capacities.

### Influence of contact time on hexavalent chromium adsorption

The influence of contact time over the adsorption of metal ions was analyzed in changing the contact time. The experiment was carried out by varying the period from 20 to 160 min by fixing the other parameters at optimum condition. Figure 3 explained that the adsorption process was in increasing trend as the time increased. This pattern might be explained by the statement that adsorbent sites were originally completely unoccupied and solute concentrations were high [13].

As time passes the surface sites become exhausted and equilibrium was attained within 80 min for both adsorbents. It was further observed that any additional amplification in contact time did not show any implication on adsorption of metal ion. At 80 min of contact time 90% removal was achieved with 18.002 mg/g adsorption capacity of activated carbon of *M. zapota*. At the same time 87% removal percentage with 13.920 mg/g adsorption capacity were encountered with activated carbon of de-oiled soya.

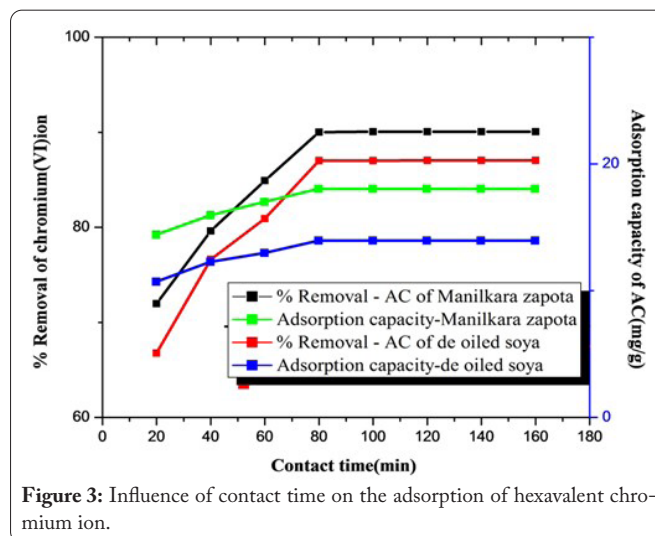


Figure 3: Influence of contact time on the adsorption of hexavalent chromium ion.

### Effect of initial concentration in hexavalent chromium adsorption

A certain amount of adsorbent may adsorb only a certain amount of heavy metal ions. Experiments were carried out for the concentration of 10 to 80 mg/L of adsorbate solutions of 100 ml volume were equilibrated against the dose of 0.2 g of *M. zapota* and 0.25 g of de-oiled soya. An increase in adsorption was reflected due to the decrease in the initial concentration of hexavalent chromium in aqueous solution which was witnessed from figure 4. Gradual improvement in the percentage removal from 61.76% to 92.54% was observed as the initial concentration reduced from 80 mg/L to 10 mg/L for activated carbon of *M. zapota* [18]. A similar trend was observed for de oiled soya also (60.76% to 90%). At lower concentration the fraction of activated sites to the overall metal ion in the wastewater solution will be high.

However, in the two adsorbents produced in this investigation, the adsorption capacity was increased at greater



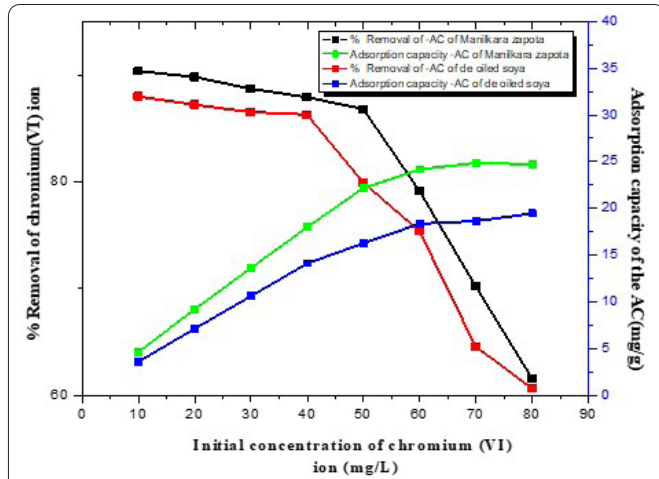


Figure 4: Influence of initial concentration on the adsorption of hexavalent chromium ion.

starting adsorbate concentrations. The findings showed that the adsorbents had an excellent adsorption capability, as shown in figure 4.

### Adsorption isotherm models of hexavalent chromium adsorption

Langmuir isotherm and Freundlich isotherm adsorption models are the most extensively utilized adsorption studies. In this work, the fitness of isotherms, pseudo-first order, and pseudo-second order adsorption kinetics was investigated. The adsorption isothermal constants were displayed in table 2. The Langmuir adsorption isotherm (Figure 5) was drawn with  $C_e$  and  $C_e/q_e$  in X- and Y-axes, respectively. By referring to Langmuir isothermal equation 1, the Langmuir constants were derived from the plot shown in figure 5.

$$\frac{C_e}{q_e} = \frac{C_e}{Q_o} + \frac{1}{bQ_o} \quad (1)$$

Similarly, the Freundlich adsorption isotherm (Figure 6) was drawn with  $\log C_e$  and  $\log q_e$  in X- and Y-axes correspondingly by keeping in view of its equation 2.

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (2)$$

$R_L$  was calculated using equation 3.

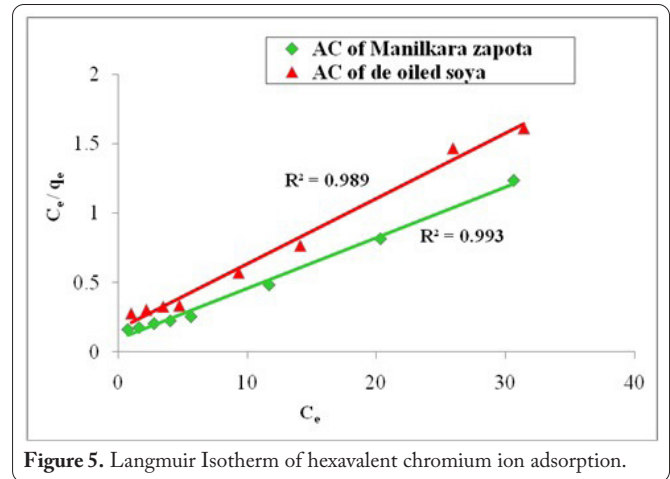


Figure 5. Langmuir Isotherm of hexavalent chromium ion adsorption.

$$R_L = \frac{1}{1 + [bC_o]} \quad (3)$$

From table 2 it was well known that the Langmuir isotherm dimensionless separation factor  $R_L$  was 0.059 and 0.082 of the two adsorbents, which were in between 0 and 1 ( $0 < R_L < 1$ ) [19-22]. This signified the feasibility of the hexavalent chromium adsorption process for all developed activated carbons. Similarly, the  $R^2$  of both adsorption isotherms was nearing 1 for both activated carbons (Figure 5 and figure 6), which revealed the adsorption was favorable and both Langmuir and Freundlich adsorption isotherm model were much appropriately fit for the hexavalent chromium adsorption study.

The slope and intercept of the curve  $C_e$  against  $C_e/q_e$  in figure 5 were used to calculate  $Q_o$  and  $b$ . The intensity of adsorption  $b$  was 0.281 and 0.396 L/mg for activated carbons of de-oiled soya and *M. zapota*, respectively, bestowing to the Langmuir isotherm model. In the elimination of hexavalent chromium ion, the highest adsorption capacities ( $Q_o$ ) of activated carbon of de-oiled soya and *M. zapota* were 21.277 mg/g and 27.778 mg/g, correspondingly.

The slope and intercept of the curve in figure 6, which was between  $\log C_e$  and  $\log q_e$ , assisted to compute the Freundlich adsorption isotherm parameters. The  $K_f$  values were 7.621 and 5.117 mg/g of the activated carbons, respectively. The

Table 2: Adsorption isotherm constants of hexavalent chromium ion adsorption.

	Activated carbon developed from <i>M. zapota</i> tree wood	Activated carbon from de-oiled soya
<b>Langmuir constants</b>		
$Q_o$ (mg/g)	27.778	21.277
$b$ (L/mg)	0.396	0.281
$R_L$	0.059	0.082
$R^2$	0.993	0.989
<b>Freundlich constants</b>		
$K_f$ (mg/g)	7.621	5.117
$n$	2.32	2.252
$R^2$	0.826	0.842

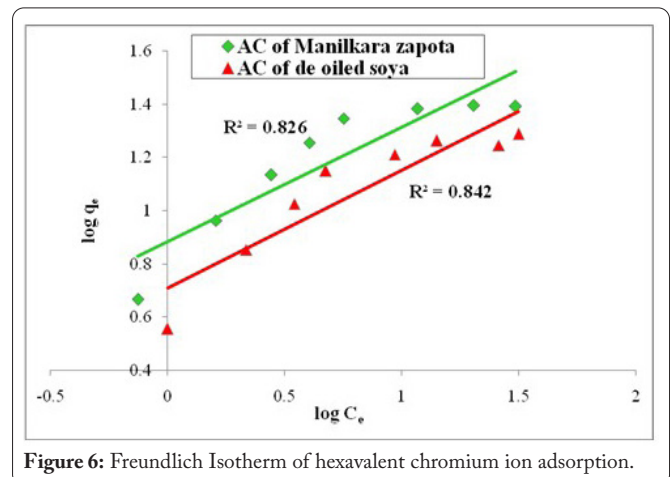


Figure 6: Freundlich Isotherm of hexavalent chromium ion adsorption.

adsorption intensities  $n$  was 2.320 and 2.252 which was greater than 1 [18] and less than 10 indicating the existence of favorable adsorption condition in the removal of hexavalent chromium with both adsorbents.

### Adsorption pseudo kinetic models of hexavalent chromium adsorption

The kinetic models of pseudo-first and pseudo-second order were exhibited in figure 7 and figure 8 with plots  $\log(q_e - q_t)$  vs time  $t$  and  $t/q_t$  and time  $t$ , respectively. The kinetic plots were drawn by employing equation 4 and equation 5. Pseudo-first order adsorption kinetic model is symbolized by equation 4.

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t \quad (4)$$

The equilibrium adsorption capabilities and at time  $t$ , respectively, are  $q_e$  and  $q_t$  in mg/g. In  $\text{min}^{-1}$ ,  $k_1$  is the pseudo-first order adsorption model constant. Equation 5 expresses the linear version of the pseudo-second-order kinetic model.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} = \frac{t}{q_e} \quad (5)$$

Where  $k_2$  indicates rate constant in  $\text{min}^{-1}$ .

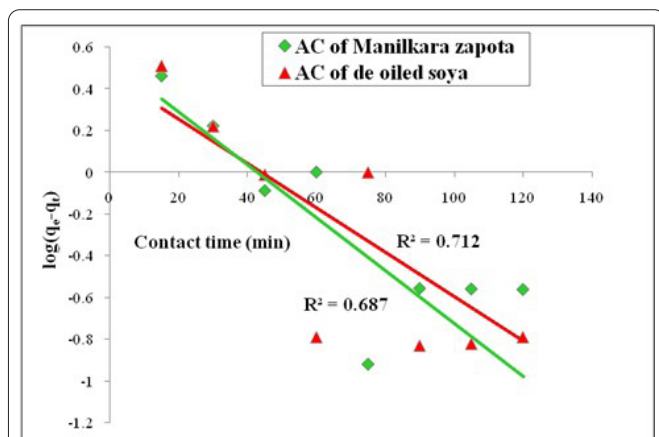


Figure 7: Pseudo-first order kinetic model of hexavalent chromium ion adsorption.

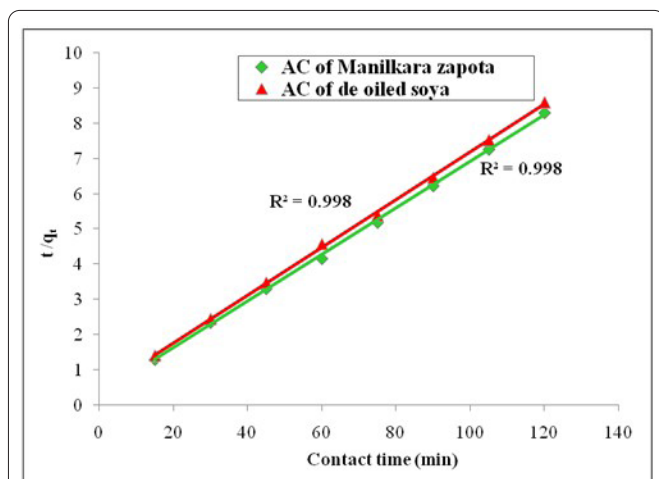


Figure 8: Pseudo-second order kinetic model of hexavalent chromium ion adsorption.

Through figure 7,  $R^2$  value of pseudo-first order adsorption kinetic model was 0.687 and 0.712 of activated carbon of de-oiled soya and *M. zapota*, respectively. Likewise, from figure 8,  $R^2$  values of pseudo-second order kinetic model was 0.998 for both carbons which depicted that hexavalent chromium adsorption perfectly fit better on the pseudo-second order kinetic model than pseudo-first order kinetic model for both activated carbons. The adsorption kinetic parameters were displayed in table 3 which were acquired from the plots in figure 7 and figure 8. The pseudo-first order kinetic parameter  $k_1$  was  $0.028 \text{ min}^{-1}$  and  $0.023 \text{ min}^{-1}$  for activated carbon of de-oiled soya and *M. zapota*, respectively, and  $q_e$  were 3.516 and 6.761 mg/g, respectively. The pseudo-second kinetic parameter  $k_2$  was  $0.019 \text{ min}^{-1}$  and  $0.021 \text{ min}^{-1}$  for activated carbon of de-oiled soya and *M. zapota*, respectively, and  $q_e$  were 13.880 and 11.880 mg/g, respectively.

Table 3: Pseudo kinetic adsorption constants of hexavalent chromium ion adsorption.

	Activated carbon of <i>M. zapota</i>	Activated carbon of de-oiled soya
<b>Pseudo-first order kinetics</b>		
$k_1(\text{min}^{-1})$	0.023	0.028
$R^2$	0.695	0.712
$q_e$ (mg/g)	3.516	6.761
<b>Pseudo-second order kinetics</b>		
$k_2$ ( $\text{min}^{-1}$ )	0.021	0.019
$R^2$	0.998	0.998
$q_e$ (mg/g)	13.88	11.88

## Conclusion

The activated carbon created from de-oiled soya and *M. zapota* proved to be an effective adsorbent for adsorbing the hexavalent chromium ion from aqueous solution. Lower pH and a greater starting concentration of chromium ion of hexavalent solution improved adsorption capability. Higher adsorbent doses and longer contact times resulted in greater adsorption capability. The  $R^2$  value of isothermal equilibrium models like Langmuir and Freundlich isotherms was approximately 1, indicating that both adsorption processes utilizing the two activated carbons were ideally suited. However, the activated carbon from *M. zapota* performed somewhat better, as shown by the Langmuir isotherm, by means of adsorption capacities of 27.778 mg/g and 21.277 mg/g for activated carbon from *M. zapota* and de-oiled soya, respectively. The adsorption progression was best suited by a pseudo-second order kinetic model. It was said at the onset that hexavalent chromium might be extracted from wastewater by using activated carbon made from de-oiled soya and *M. zapota*.

## Acknowledgments

None

## Conflict of Interest

None

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