Langmuir, Freundlich and Tamkin Adsorption Isotherms and Kinetics For The Removal Aartichoke Tournefortii Straw From Agricultural Waste

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Abstract

The research, concerned with Chromium (VI) removal from wastewater using magnetic nano composite. Effect of the active carbon nano composite on Chromium (VI) adsorption from water was measured in terms of various parameters such as absorbent dose, Chromium (VI) concentration, pH, contacts time and temperature. Activated carbon magnetic nano composite was made by mixing artichoke tournefortii straw with Fecl₃·6H₂O salt and ethanol then was burned. Our results show that produced nano composite has good magnetic properties, which optimal conditions for the removal of chromium were 50ppm of concentrations chromium (VI), 2-5 acidic pH, 0.03 gm of adsorbent dose and 25°C temperature. adsorption data in the range of pH values (2.0 3-10.04) using (Cr) concentration of (10ppm-100ppm) in solution were correlated using the liner forms of the Langmuir and Freundlich equations by using available temperatures three (25 room temperature ,35,45) To find the amount of absorbed soluble (Qₑ) at equilibrium, this research included the study of the adsorption of Chromium was estimated using the method adsorbent quantities spectroscopic device (UV) Type of (Spectrophotometer UV- Visible) (J9Sco -V- 530) and the results showed that the adsorption of Chromium follows the Langmuir equation for adsorption at a range of temperatures (25,35,45°C) and the Freundlich equation. At pH5 are the optimum conditions for excellent removal of chromium. The experimental isotherm data were analyzed using Langmuir, Freundlich and Tamkin. Tamkin is found to be the best model to present the equilibrium data. The operating lines were used to calculate the predicted values of the percent removal of chromium from solution using Tamkin isotherm. The purpose of this article is to review rather scattered information on the utilization of Gundelia for the removal of metal ions from waters.

Keywords: Magnetic activated, carbon Nano composite, Gundelia tournefortii, Chromium (VI), adsorption, isotherms, kinetics.

Introduction

Hexavalent chromium Cr (VI) is one of the higher toxic heavy metals. Cr (VI) poisoning in human beings is harmful to the nervous system, bleed, live and bone [1]. Cr (VI) is observed in
different industrial wastes including leather tanning, electroplating and metal polishing. Therefore, the removal of Cr (VI) from natural waters and wastewater is one of the great importances. Several methods condense of chemical precipitation, ion exchange adsorption, membrane filtration and solvent extraction have been used for the removal of Cr (VI) from aqueous systems [2]. Among technique, adsorption process due to its easy operation, high efficiency and low cost is commonly preferred [8]. Development of new adsorbents with simple synthesis, high specific surface area, easy separation and good chemical stability should be considered. Although the researches about chromium based adsorption materials are increasing recently. titanate nano tubes functionalized for the removal of heavy ions of Cr [9], the composite magnetic graphene and its application for the removal of chromium, lead, mercury, cadmium and nickel etc. [10]. thus with respect to environmental compatibility, economic benefit and returns of this method, the absorption of Cr (VI) from aqueous solution under different kinetic and equilibrium conditions has been investigated in detail in present study.

Materials and Methods

Chemical and material

All chemical reagents used were of analytical grade without further purification. Different concentration of Cr (VI) (10-100 ppm) were prepared and the effect of different pH (2-10) and different solutions in 25 ml from Chromium volume to the concentration 50 ppm during the adsorption process were investigated. Because of the low removal percentage in pH=10, tests continued in pH (2-9) to find the effect of contact time, the different times (20, 30, 60, 90, 120, 150, 180, 210 and 240 minutes) were selected. A discontinues method was used to determine the pollutant adsorption isotherm. First, synthetic sample with a defined Cr (VI) concentration was prepared. We solved K$_2$ Cr$_2$ O$_7$ in deionized water to prepare Cr (VI) solution. After that, different dose of adsorbent were added to sample. This container mixed for 24 hours in a condition that temperature and mixed rate were steady at (10, 20, 30, 40 and 50 ppm), respectively. Then Cr concentration in liquid phase was measured, and adsorbents equality capacities were calculated by use of formulas and graphs. Then was designate concentration of the solution when equilibrium $C_e$ (mg / L) then been calculated the amount of the adsorbent $Q_e$ (mg / g) according to the following equation:

$$Q_e = (C_o - C_e) * V / M$$

$C_c$: It shows the concentration in quality conditions (mg/l)
Q_e: It introduces the amount of adsorbats on one unite of adsorbents weight in quality conditions (mg/g)
C_o: It indicates the concentration of primary material adsorbent (mg/L).
V: the total volume of the adsorbent solution (L).
M: weight of adsorbent (g).

**Adsorption isotherm:**

Analysis of the isotherm data is necessary in order to develop an equation that can accurately represent the results and could be used for design purposes [11].

An adsorption isotherm describes the relationship between the amounts of adsorbants which is adsorbed on the adsorbent and the concentration of dissolved adsorbate in the liquid at equilibrium [13]. The parameter C_eq corresponds to the remaining metal ion concentration in the solution and Q_eq refers to the amount of metal ion adsorbed per unit weight of adsorbent.

- **Langmuir equation:**
  
  \[
  \frac{C_q}{Q_q} = \frac{1}{bQ_m} + \frac{C_q}{Q_m}
  \]
  
  b: constant isotherm langmuire
  
  Q_m: adsorption capacity, It can calculate the values of b,Q_m draw from the linear relationship between C_e / Q_e exchange for C_e that give amount of tendency 
  
  \[
  \left( \frac{1}{Q_m} \right) \text{ and section } \frac{1}{bQ_m} .
  \]
  
  The parameter C_eq corresponds to the remaining concentration of the adsorbate in the solution and Q_e is the amount adsorbed at equilibrium [14].

- **Freundlich equation:**
  
  \[
  \log Q_{eq} = \log K + \frac{1}{n} \log C_{eq}
  \]
  
  n and k: are Freundlich constant
  
  Q_e : amount of adsorbent
  
  C_e : concentration of material is not adsorbent
  
  As gives a the relationship between drawing \( \log Q_e \) Exchange for \( \log C_e \) "straight line" with tendency \( 1/n \) which represents a measure of the intensity of adsorption and amount of section( \( \log k \) ) that represents the adsorption capacity a function.

- **Tamkin equation:**
  
  \[
  Q_e = B \ln A + B \ln C_e
  \]
  
  A and B are the Tamkin constants and can be determined by a plot of Q_e versus ln C_e .

  The parameters , A and B, together with the correlation coefficient are Table 1.
Table 1.
Isotherm parameters obtained for the adsorption of Cr (VI) ions onto artichoke tournefortii straw

| Isotherm models | 25 °C | 35 °C | 45 °C |
|-----------------|-------|-------|-------|
| **Langmuir**    |       |       |       |
| $Q_m$ (mg/g)    | 49.14 | 82.29 | 102.34|
| $K_L$ (L/mg)    | 0.616 | 0.820 | 1.829 |
| $R^2$           | 0.99625 | 0.92603 | 0.98861|
| **Freundlich**  |       |       |       |
| $K_F$ (mg/g) (l/g)${}^{1/n}$ | 82.25 | 88.38 | 100.92|
| $1/n$           | 1.226 | 1.213 | 1.031 |
| $R^2$           | 0.99592 | 0.98784 | 0.99642|
| **Tamkin**      |       |       |       |
| $A$             | 3.63  | 3.69  | 3.88  |
| $B$             | 174.6 | 225.5 | 299.3 |
| $R^2$           | 0.95987 | 0.93992 | 0.94748|

The linear Langmuir, Freundlich and Tamkin plots so the calculated adsorption constants are given in (Fig 1, 2 and 3). Based on the regression correlation coefficients obtained, it was obvious that the Freundlich model ($R^2 = 0.99642$) at 45 °C fitted the adsorption data better than the Langmuir model ($R^2 = 0.98861$) at 45 °C. The result indicates that Cr (VI) adsorption on the surface of artichoke tournefortii straw from aqueous phase might not accrue in a homogeneous monolayer but a heterogeneous complex way. According to the theory of Freundlich isotherm model, the heterogeneous surface of artichoke tournefortii straw might have kinds of adsorption sites, and the affinities of these adsorption sites on the Cr (VI) are different.

**Method**

**Bath Cr (VI) adsorption experiments**

All experiments were conducted at room temperature, rotational speed of the stirrer at all stages (100rpm). Absorbance magnetic activated carbon adsorbent (MCG) in a shaker so as to ensure sufficient adsorption at ambient temperature (25, 35 and 45°C). The adsorption experiments carried out in present study were summarized in Table 2,

Table 2.
Effect of different adsorption parameters on Cr (VI) adsorption onto artichoke tournefortii straw.

| Adsorption parameters | Contact time (min) | pH  | Dosage (g L$^{-1}$) | Consternation of Cr(VI)ppm |
|-----------------------|-------------------|-----|---------------------|---------------------------|
|                       | 20                | 2.03| 0.005               | 10                        |
SEM analysis

The adsorbent was characterized by SEM scanning electron micrographs (SEM) of the samples were characterized FEI Quanta FEG 200 High resolution SEM). Surface morphology of magnetic activated carbon adsorbent (MCG) were carried out by SEM analysis and it was shown in (Figure 1). Magnetic activated carbon adsorbent (MCG) were uniform in size and spherical in shape and the average size of (MCG) is between 20-30 nm. The aggregation is attributed to the magnetic force among the iron particles [15].

| Time (s) | SEM Value | FTIR Value |
|---------|------------|------------|
| 30      | 3.03       | 0.007      |
| 60      | 4.05       | 0.009      |
| 90      | 5.01       | 0.01       |
| 120     | 6.02       | 0.03       |
| 150     | 7.03       | 0.05       |
| 180     | 8.03       | 0.07       |
| 210     | 9.12       | 0.09       |
| 240     | 10.04      | 0.1        |

FTIR analysis

The FTIR spectra were sketched beside wavenumbers extending from 500-4000 cm\(^{-1}\) at the x-axis so % transmittance at the y-axis (Figure 2). The prominent bands in pristine Straw Artichoke (GS) were at 1616.09 cm\(^{-1}\) (C-H stretching vibration), 556.59 cm\(^{-1}\) (C-H stretching vibration), 2384 cm\(^{-1}\) Straw Artichoke (GS) exhibit adsorption bands at 1570 - 500 , 1616.09 , 556.59 , 457.38 cm\(^{-1}\) The wide and strong absorption bands in the region of 1570 – 500 was
attributed to O-H stretching vibration. The band at 558 cm\(^{-1}\) was attributed to O-H stretching of water molecules. (16). The spectrum was sketched employing the similar system on the transmittance axis for total the adsorbents. The FTIR spectra of the adsorbents exhibit the number of adsorption summits, showing the difficult nature of the prepared adsorbents. The absorption summits about 1616.09 cm\(^{-1}\) show the existence of clear and intermolecular bonded hydroxyl groups. Summits recognized at 556.59 cm\(^{-1}\) can be assigned to the C-H stretching oscillation of the (-CH2-) group. The peaks around 457.38 cm\(^{-1}\) agree to the carbonyl group in a quinone as well as representing a γ-pyrone structure beside big oscillations from a mixture of C=O and C=C [16]. The chemical composition of Straw Artichoke (GS) as obvious from FTIR spectrum shows that Straw Artichoke (GS) is the best sorbent for element binding.

![FTIR spectra of native Straw Artichoke (GS)](image)

**FIGURE 2.** FTIR spectra of native Straw Artichoke (GS)

**Effect of temperature on the adsorption isotherm of Straw Artichoke (GS)**

The adsorption isotherms of Straw Artichoke (GS) at different temperature are presented in Figure 3, 4 and 5. It can be seen that all the adsorption isotherms are of the typical Langmuir, Freundlich and Tamkin. Table1. Summarize all the constants and the coefficient of determination ( \( R^2 \) ) values of the three isotherm models used in the study. The Langmuir, Freundlich and Tamkin models yielded the best fits. Conformation of the experimental data with Freundlich isotherm equation indicates the heterogeneous nature of surface (Figure 4). Its mean the activation energy varies as a function of the surface coverage[15-19]. The finding also
demonstrate the formation of heterogeneous coverage of Cr (VI) molecule at the outer surface of Straw Artichoke. From the fitting of Langmuir isotherm model (Figure 3), the adsorption capacity ($Q_m$) of Straw Artichoke might be due to variation in the original nature of the adsorbents, the modifications or processes applied to produce the adsorbents as well as the conditions used during the adsorption processes.

**FIGURE 3.** Langmuir isotherm of Chromium at (25,35,45 °C)

**FIGURE 4.** Freundlich isotherm of Chromium at (25,35,45 °C)

**FIGURE 5.** Tamkin isotherm of Chromium at (25,35,45 °C)

**Conclusion**

Removal of Chromium (VI) from solution was possible using selected adsorbents. Straw Artichoke was effective for which the removal at concentration of 50ppm at pH = 4.05. Equilibrium isotherm data fitted well to the Freundlich isotherm model. The Straw Artichoke adsorbent showed its usefulness in real wastewater treatment by removing Cr (VI) from mining industry wastewater contaminated with other metal ions. It was found that the percentage adsorption of Cr (VI) decrease with the increase in the initial Cr (VI) concentration. This was expected due to the fact that for a fixed adsorbent dosage. Thus from the use of Straw Artichoke
reductive efficacy of Cr (VI) contaminated water can be done which is evidenced by the results from present research.

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