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Removal of Hexavalent Chromium (Cr^{6+}) Using Different Natural Adsorbents-A Review

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Abstract

Heavy metal is one of the major environmental and ecological problems in this world. The presence of heavy metals in water and wastewater causes toxic effects to the living beings and the environment. Compared to other heavy metals (such as Cr^{6+}, Pb^{2+}, Zn^{2+} etc.,) Chromium found in the tannery and electroplating industrial effluents causes serious effects to the humans and living organisms. It also contaminates the soil and groundwater. The excess amount of chromium affects the lungs and lead to respiratory disorders in the human beings. Due to a large number of tanneries and electroplating industries, the chromium contamination in the wastewater and aqueous solutions exceeds the tolerance limits. Many methods are used to remove the chromium from the aqueous solutions and industrial effluents. Adsorption is one of the cost - effective methods being widely used for the removal of heavy metals from industrial and commercial wastewaters. It has been established as an important and economically feasible treatment technology for removing heavy metals, particularly chromium. This review article presents the information about the application of different kinds of natural waste adsorbents for the removal of hexavalent chromium (Cr^{6+}) from industrial effluent.

Keywords: Adsorption; Natural adsorbents; Factors of efficiency; Hexavalent chromium (Cr^{6+})

Introduction

Chromium is a brittle and hard material. The Colour of chromium is grayish silver and highly polished in nature. The chromium is mined from the chromites ($FeCr_2O_4$) ores obtained below the earth's crest. It has high hardness value and corrosion resistance, mainly used in the manufacturing of stainless steels. The average concentration of chromium in the earth's crust is 100 ppm [1]. When the chromium is heated up, it forms a chromic acid which is green in colour and it could not be stable. The level of the chromium in air and water is very low compared to the contaminated water. Chromium exists in two forms namely 1. Hexavalent Chromium (Cr^{6+}), 2. Trivalent Chromium (Cr^{3+}). Trivalent Chromium (Cr^{3+}) naturally accumulates in fruits, vegetables and meat. Also, it is one of the essential nutrients for human beings. But too much of trivalent chromium causes skin rashes and other harmful diseases. Comparing the trivalent and the hexavalent chromium, the latter is highly dangerous, and it causes serious effects (Lung Cancer, Headache etc.,) to the human health. At the low or neutral pH values, the Cr^{6+}compounds are the powerful oxidants. The mechanism of oxidation by Cr^{6+} is presented in Equation 1.

$$2[CrO_4]^{2-} + 2\,H^{+}=[Cr_2O7]^{2-}+H_2O \qquad (1)$$

The toxicity level of the chromium ranges between 50-150 µg/kg [2]. Removal of toxic level of the chromium content from the water and wastewater is a complicated process and the cost of this process is very high. A wide range of treatment methods is (Adsorption, Ion exchange, chemical precipitation etc.,) available to reduce the heavy metal toxicity levels from the water and wastewater [3]. Ion exchange, Adsorption and Precipitation are the most efficient methods used to remove the heavy metals from the wastewater [4].

Adsorption is the process of transferring the ions from solution phase to solid phase. In this process a film called adsorbent surface is created. There are two types of adsorption, 1. Physical Adsorption (Physisorption) and 2. Chemical Adsorption (Chemisorption). The Physical Adsorption can be used only in the temperature ranges from 20-40 KJ/Mol, But the chemical adsorption may use at the high temperature ranges from 40-400 KJ/Mol. Compared to physical adsorption technique, the chemical adsorption requires separate activation energy for transferring the atoms into the adsorption surface.

The Adsorption isotherm is the graphical representation, which is used to study the amount of adsorbate and adsorbent and its concentration at a constant temperature [5]. In this paper, a review of different kinds of natural adsorbents to reduce the toxicity level of the hexavalent chromium (Cr^{6+}) is studied. Here, adsorbents (a substance which adsorbs another) [6-10] have been used to receive the metal ions from the water and wastewater. The Adsorption isotherms and kinetic studies were not considered in the papers reviewed have only dealt with adsorption at room temperature. Hence, the factors affecting the adsorption efficiency (Effects of pH, Contact time, Concentration etc.) has been widely discussed in this review paper.

Various Natural Adsorbents

Coconut shell

Coconut shell was used as an adsorbent to remove the Chromium (Cr^{6+}) from the effluent. Batch adsorption process and column studies were conducted and finally the fraction was adsorbed in the following different categories at the room temperature [11-14].

pH: The maximum adsorption of Hexavalent chromium (83%) was achieved at the pH of 1.5. Here, the pH had been adjusted from 1.5 to 7 and due to this adjustment; the efficiency of Hexavalent Chromium had gradually decreased to 36%. The reason for this decrease is that at low pH values the presence of H+ ions are attracted by the negatively charged hydroxyl group (-OH) on the adsorbed surface.

Adsorbent dose: The hexavalent chromium removal efficiency achieved was up to 88.28% with an adsorbent dose of 15 gm/L. In this work, the efficiency gradually increased from 53.3% to 84.1% when the dose is increased up to 10 gm/L. From this, it is certain that the efficiency has been strongly dependent on the adsorbent dose. When the adsorbent dose is increased the removal efficiency of heavy metal has also increased.

Initial concentration: The concentration had been adjusted from 5-100 gm/L. Here, the maximum removal efficiency attained was up to 87.3% at the concentration of 50 mg/L. When, the concentration of chromium was increased the removal efficiency was gradually decreased.

Contact time: The contact time of the removal efficiency of hexavalent chromium depends upon the size of the particles. In this work the particle size used were (75 um-600 um) in different levels at an initial adsorbate concentration of 50 gm/L. The maximum removal efficiency was attained for 75 um particle size and its contact time was 10 hours and after that, it remained constant.

Particle size: The size of the particle was also one of the major characters for adsorption of heavy metals. When the size of the particle was high, the adsorption efficiency had decreased. In this work, the particle sizes in different ranges (75 um-600 um) were analyzed and the maximum efficiency (83%) was attained at the particle size of 75 um and the efficiency got decreased when the size of the particle is decreased.

Saw dust

In this work, the aqueous solution was used to remove the hexavalent chromium by using sawdust. The solution was prepared by dissolving the potassium dichromate (99.9%) in 1000 mLof distilled water and the pH was adjusted by 0.5 N of HCL and 0.5 N of NaOH Solution [10]. Batch adsorption technique was used and the removal efficiency of Cr^{6+} had been discussed in the following manner.

pH: Adsorption of Cr^{6+} adjusting the pH (1-11) was studied in this work and the removal efficiency of Cr^{6+} was found an increase to after the pH value of 6.9, The maximum removal efficiency was attained at the pH of 1.

Contact time: when the efficiency had reached the maximum (pH=1), the initial concentration of Cr^{6+} was adjusted to a range of 100-400 mg/L. Due to this reason, the efficiency slowly decreased from 86% to 66% for the contact time of 250 minutes But, till 1050 minutes of contact time the removal efficiency had changed from 99% to 81%.

Adsorbent dose: The removal efficiency of Cr^{6+} was increased from 98.3% to 99.8% when the amount of adsorbent was increased from 4 gm/L to 24 gm/L also the adsorption capacity decreased from 12.28 mg/g to 2.06 gm/g. Here, the optimum value was found at 8.7 mg/g for 99% of adsorption efficiency of Cr^{6+}.

Initial concentration: The concentration was adjusted from 50-500 mg/g in this work and due to this reason, the removal efficiency was decreased from 99.9% to 89% and also it reaches the maximum adsorption capacity from 4.98 to 41.45 mg/g.

Particle size: This is one of the major parameters for adsorption technique. In this work, the size of the particle was not taken into consideration. When the size of the particle was increased the adsorption, efficiency got decreased.

Coconut shell charcoal

Electroplating Industrial effluent was used to remove the Cr^{6+} by using the coconut shell charcoal as an adsorbent. The chromium adsorption was obtained by the source using potassium dichromate (0.7071 gm of $K_2Cr_2O_7$ dissolved 500 mL of deionized water. Batch adsorption technique was used, and the chromium adsorption has been discussed in the following categories [15-20].

pH: The efficiency of the Cr^{6+} was analyzed with varying pH (2-9) values. In this work, the efficiency was increased from 75% to 86% at the pH value from 2 to 6. After that, the efficiency gradually decreased from 85% to 33% at the pH value from 6.5 to 9.

Contact time: Increasing the removal efficiency from 60% to 87% for a contact time 30 to 180 minutes the efficiency attained a constant value.

Adsorbent dose: The adsorbent dosage was increased from 1.5 gm/L to 25.5 gm/L and the other parameters (pH, Contact time etc.) were kept constant. Here, the efficiency of the chromium removal increased at a dosage of 20 mg/L, after that the efficiency remained constant.

Initial concentration: The concentration of chromium was adjusted from 5 mg/L to 25 mg/L. The maximum adsorption efficiency gradually decreased when the concentration decreased.

Particle size: The size of the adsorbent particles was within the range of 0.42 mm to 1.70 mm. In this work, different sizes of adsorbent particles were used at the same time.

Agricultural waste

Used aqueous solution to remove the Cr^{6+} by using Activated Carbon Rice straw as an adsorbent. In this work, the chromium was introduced by adding potassium dichromate in distilled water with the concentration from 1.5 to 5 mg/L. The batch adsorption process was carried out and the efficiency of the removal of Cr^{6+} had been discussed in the following manners [21-24].

pH: The efficiency of removal of chromium was carried out at different pH (2 to 8) intervals with initial chromium concentration of 1.5 mg/L. Here, the maximum removal efficiency (96.72%) was attained at a pH of 8. When the pH was decreased the adsorption efficiency also decreased.

Contact time: The chromium removal was high at the initial stages and after 100 minutes the removal efficiency attained a constant value. From then, the removal was dependent on the concentration.

Adsorbent dose: The dose had been adjusted from 2 gm/L to 9 gm/L. due to which the removal efficiency of Cr^{6+} has considerably increased from 45% to 97.12%.

Initial concentration: The concentration of chromium was adjusted from 1.5 mg/L to 5 mg/L. Due to this reason the adsorption efficiency had been decreased from 76% to 46%.

Particle size: The adsorbent particle sizes are 100, 150 and 200 μm were taken for the removal of chromium and it has been found that the efficiency gradually decreased from 79.2% to 53.3% with the initial concentration of Chromium (1.5 mg/L) [25-28].

Neem leaves

The aqueous solution was used to remove the Cr^{6+} by using the Neem leaves powder as an adsorbent. Chromium chloride was prepared, and it is dissolved in distilled water. Batch adsorption technique was conducted and the removal efficiency of Cr^{6+} had been discussed in the following manner [29-32].

pH: The maximum removal efficiency (67.5%) was attained at an optimum pH of 4.1, after that it slowly decreased.

Initial concentration: The maximum removal efficiency was attained at 98% at an initial concentration of 30 mg/ 100 mL. when the initial concentration increases the amount of adsorbent material gradually falls down.

Adsorbent dose: The removal efficiency of chromium increased when the adsorbent dose has been increased (2 gm /100 mL to 10 gm/100 mL). The maximum removal efficiency (85%) was obtained at the dosage level of 8 gm/ ml, after that remained constant.

Contact time: The effect of contact time was not properly discussed in this research work. But, with reference to the graph the maximum removal efficiency (67.5%) was attained at the time of 80 min and after that the efficiency was constant.

Particle size: The size of the adsorbent particle was not discussed clearly in this work. But, the particle size plays the major role in the adsorption efficiency of heavy metals from the wastewater.

Banana peels

Banana peels were used as an adsorbent to remove the Cr^{6+} from the aqueous solution. Here the banana peels were treated with 10% of HCL and 10% of NaOH solutions and washed by distilled water for neutralization. The process of adsorption was carried out using potassium dichromate ($K_2Cr_2O_7$) solution [33-40]. Batch adsorption technique was used, and the removal efficiency of the chromium had been discussed in the following categories.

pH: The efficiency of the chromium removal was attained a maximum level of 96% at the pH of 3. After that, the efficiency slowly decreased, and it remained constant at the pH of 8.

Initial concentration: The concentration of bleached pulp was adjusted from 0.5 gm to 3.5 gm/10 gm. In this concentration, the efficiency had increased considerably. When the concentration was higher (4 gm) the efficiency had a constant value.

Contact time: The maximum removal efficiency was obtained for the first 60 minutes and the time had been increased up to 2 hours, but the efficiency was constant at an optimum pH of 3.

Adsorbent dose: The adsorbent dose was added at different levels (1 gm/L to 5 gm/L) at a constant solution level of 400 mg/L having pH=4. Here the chromium removal was increased when the adsorbent dose was increased. The dose level of 5 gm/L gets the maximum efficiency and after that, it remained constant.

Particle size: In this work, the size of the particles was not considered for adsorption efficiency. But, it is one of the parameters which affected the heavy metal adsorption [41-45].

Bamboo waste

In this work the bamboo waste was used as an adsorbent to remove the chromium content from the aqueous solution. The bamboo wastes were treated with potassium hydroxide solution after that it was cleaned with HCL solution. The process of adsorption was carried out using potassium dichromate ($K_2Cr_2O_7$) solution [46-50]. Batch adsorption technique was used, and the removal efficiency of the chromium has been discussed in the following categories.

pH: The maximum chromium adsorption (98.28%) was attained at the pH of 2, and an increase in the pH value, the efficiency of the adsorption gradually decreased.

Initial concentration: The concentration was adjusted from 25 mg/L to 150 mg/L. Due to this, the adsorption efficiency of hexavalent chromium increased from 92.87% to 98.71% and the solution had reached its equilibrium at 100 mg/L.

Contact time: The maximum removal efficiency was attained at 3 minutes and it was maintained up to 20 minutes at a concentration of 100 mg/L. After that, the efficiency gradually decreased, and it attained the saturation level.

Adsorbent dose: The adsorbent dose was added at different levels (0.1 gm to 0.30 gm) to a constant solution level of 100 gm/L. The removal efficiency was gradually increased when the dose was increased. The maximum adsorption (98.45%) was attained at the dose level of 0.25 gm, after that the efficiency gets constant.

Particle size: Fine particles were used in this work and the size is even (150 μm). Due, to this even size there is no significant change in efficiency of chromium adsorption.

Green tea leaves

Green tea leaves were used to remove the hexavalent chromium from the aqueous solutions. Potassium dichromate was used as a stock solution, batch adsorption studies were carried out and the removal efficiency of hexavalent chromium fraction has to be discussed in the following categories [51-56].

pH: The maximum adsorption efficiency (92%) was achieved at the pH of 2, and after that the efficiency rate was gradually decreased when the pH of the solution was adjusted (3-10). The adsorption of chromium was not efficient after the pH of 6.

Contact time: The test was carried out from 30 minutes to 300 minutes. But, the maximum adsorption efficiency was reached at 180 minutes and after that, the efficiency was gradually decreased, and it attains the constant value.

Initial concentration: The concentration of chromium was adjusted from 5 mg /L to 500 mg/L. the maximum adsorption efficiency was attained at the concentration of 10 mg/L. After that, the efficiency was slowly decreased when the concentration increases and after that it attains the equilibrium.

Adsorbent dose: The maximum removal efficiency of 96% was attained at the adsorbent dose level of 0.8 gm/L. After that, the adsorption efficiency goes to the constant value and there are no any significant changes in the efficiency of chromium.

Particle size: 540 nm size particles were used in this work. But, the effect of adsorption was not discussed in detail. Size of the particle is one of the characters which affect the adsorption efficiency [57,58].

Grape leaves activated carbon

In this work, grape leaves was used as an adsorbent for the removal of hexavalent chromium from the aqueous solution. The removal efficiency of chromium from potassium dichromate stock solution was discussed in the following categories [59-63].

pH: The maximum adsorption efficiency (89.5%) was attained at the pH of 1.5, and when the pH was adjusted from 1.5 to 9 the efficiency decreases gradually, and it goes to constant value.

Contact time: The test was carried out from 10 minutes to 120 minutes. Here, the maximum adsorption was carried out within the time range of 60 min to 90 min, a ter that it goes to equilibrium status.

Initial concentration: The metal ion concentration was adjusted from 25 mg/L to 200 mg/L. chromium efficiency was reached at the maximum level when the concentration is 25 mg/L, after that the efficiency decreases and goes to constant value.

Adsorbent dose: The adsorbent dose was added to the adsorption bed with the range of 0.2 gm to 3 gm. Due to the excess amount of concentration, the efficiency of the adsorption was gradually decreased (85.5% to 82%).

Particle size: The size of the particle was not measured in this work because of the adsorbent was in the form of powder. The weight of the powder was 0.3 gm used for this work.

Groundnut hull

Groundnut hull was used as an adsorbent for the adsorption of hexavalent chromium from the aqueous solution. The groundnut hull was used in two different types for the adsorption. 1. MGS (Modified Groundnut Shell), 2. UGS (Unmodified Groundnut Shell). Potassium dichromate was the stock solution for chromium adsorption and batch adsorption technique had been used and the efficiency of chromium adsorption was discussed from the following various adsorption parameters [64,65].

pH: The adsorption of chromium using MGS and UGS was investigated in different pH levels (1 to 8). At the pH of 2, two different adsorbents were given their best removal efficiency of chromium, but compared to UGS (82%), The MGS was given the maximum removal efficiency (96%) of the hexavalent chromium. When the value of pH increases the efficiency of chromium was gradually decreased and it attains the equilibrium.

Contact time: In this work the maximum adsorption efficiency was attained at 30 minutes for both the adsorbents (UGS, MGS). But, after that the efficiency gets equilibrium state. The adsorption gets the equilibrium state for both the adsorbents (UGS, MGS) at 60 minutes and 80 minutes time level and after that, the efficiency was gradually decreased [66].

Initial concentration: The concentration was adjusted from 0 to 25 mg/L. The maximum adsorption efficiency was observed that 18 mg/L concentration of chromium and after that it goes to equilibrium for MGS. But, the removal efficiency of chromium was attained at the maximum level when the concentration was in 8.3 mg/L for UGS.

Adsorbent dose: The adsorbent dose was adjusted from 5 to 40 mg. Due to these adjustments of dose levels, the adsorption efficiency of chromium was gradually increased gradually (UGS- 88% MGS -98%).

Particle size: The MGS and UGS are used as adsorbents in the form of powder. The size of the adsorbents was in the range of 200-300 µm. Due to this even size, there is no significant change in the adsorption efficiency of chromium [67].

Conclusion

Hexavalent chromium (Cr^{6+}) is more toxic in nature compared to the trivalent chromium (Cr^{3+}). Many industries such as Electroplating, Tanneries etc., have been discharging high amount of Hexavalent chromium (Cr^{6+}) in their effluents [68]. Conversion of Hexavalent chromium (Cr^{6+}) into the trivalent chromium (Cr^{3+}) is more costly and time consuming process. From this review, it is concluded that sawdust is the best adsorbent to remove the Hexavalent Chromium (Cr^{6+}) with an efficiency of 99.9%. Here, the saw dust plays a major role in adsorption and accumulation of heavy metal contents from the wastewater [69,70]. Due to its organic nature and high amount of carbon content [66] (48.98%), it can be easily adsorbed the different types of heavy metals in both liquid and gaseous states. Also, the Banana Peels (98%), Bamboo waste (98%) and Agricultural waste (98%) had given their best adsorption rate of Hexavalent Chromium (Cr^{6+}). However, these efficiencies are obtained from the aqueous solutions, not industrial effluents (Because of high concentration). Combination of these adsorbents in equal or different ratios will give the maximum efficiency (100%) of removal of Hexavalent Chromium (Cr^{6+}) from the industrial effluent such as tanneries, electroplating industries etc.

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