The Use of Tea leaves Wastes to reduce Hexavalent Chromium Concentration in industrial Waste Water by Adsorption

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Abstract :

A research was conducted to study the process parameters affecting hexavalent chromium Cr (VI) (carcinogenic compound) the removal percentage from the electrical industries company waste water that contain 88 mg/l of Cr (VI) concentration by adsorption onto tea wastes. Synthetic water with 88 mg/l Cr (VI) concentration was used. Several operation parameters affecting Cr (VI) removal efficiency were investigated, such as pH, initial Cr (VI) concentration, stirring time and tea wastes dose. The experimental results reveal that maximum Cr (VI) removal reached up to 94.26% at pH of 2, stirring time of 180 minute, tea wastes dose of 8gm/100 ml and the equilibrium was attained at 180 minute. Langmuir and Freundlich adsorption isotherm models were analyzed and the experimental results fit very well with Freundlich model.

Key words: Adsorption; Removal efficiency; Hexavalent chromium; Tea wastes; Isotherm

Introduction:

The presence of heavy metals in drinking water sources and in edible agricultural crops is harmful to human beings. It is well known that heavy metals are toxic, e.g. they damage nerves, liver and bones also they block functional groups of vital enzymes [1]. Chromium a highly reactive metal and its compounds are being intensively used in modern industries such as textile, dyeing, leather tanning, electroplating and metal finishing, and these results in the discharge of good quantities of chromium compounds through effluents into the environment [2, 3, 4]. Chromium is present in trivalent and hexavalent forms in industrial wastes [5]

Cr (VI) is more hazardous to biological activities, its compounds are carcinogenic and corrosive on tissue and long-term exposure causes nausea, ulceration, skin sensitization and kidney damage [4, 6, 7]. Hexavalent chromium which is primarily present in two forms of chromate (CrO_4^{-2}) and dichromate ($Cr_2O_7^{-2}$) possess significantly higher levels of toxicity in comparison with other valence state [8]. Various industrial processes involve the use of Cr (VI), such as steel production, electroplating, leather tanning, nuclear power plants, textile industries, wood preservation, anodizing of aluminum, water-cooling and chromate preparation. Discharge of wastes containing chromium occurs into environment, with its varied concentration between 5 and 220 mg/L, such discharge ultimately contaminates soil and water [9]. The tolerance limit for the discharge of Cr (VI) into inland surface water is 0.1

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mg/l and in potable water is 0.05 mg/l [10].

Different methods such as reduction and precipitation, ion exchange, electrolysis, reverse osmosis, solvent extraction, adsorption and electrochemical precipitation have been suggested for the removal of Cr (VI). Among all these, adsorption to be a highly effective and the most promising technique and a feasible alternative [11, 12, 13].

Aim of Research:

The aim of this research is to study the ability of tea leaves wastes for hexavalent chromium adsorption from water and to investigate the effect of different operation conditions on hexavalent chromium removal efficiency.

Materials and Methods:

Adsorbate (hexavalent chromium)

The stock solution of hexavalent chromium Cr (VI) was prepared by dissolving 2.828 gm of analytical grade of potassium dichromate ($K_2Cr_2O_7$) procured from Fluka Company, in 1000 ml of distilled water. The stock solution is further diluted with distilled water to reach the desired concentration for adsorption measurement. pH adjustment is carried out by using sulphuric acid.

Adsorbent (Waste tea leaves)

Waste tea leaves were washed several times with boiling water to remove the present soluble and colored compounds until the filtrate was virtually colorless. The washed waste tea leaves were dried at a temperature of 110 ^oC, and then the dried leaves were grind to be a powder.

Analysis of hexavalent chromium concentration

The concentration of hexavalent chromium was analyzed by Atomic Absorption flame Emission Spectrophotometer (AA-6200), Shimadzu (Japan).

Experimental procedure

Batch adsorption was carried out to obtain equilibrium data and investigate the effect of pH, mixing time, initial Cr (VI) concentration and adsorbent dose on hexavalent chromium removal at the temperature held at 19^{o}C in a laboratory batch unit.

To investigate the effect of pH of hexavalent chromium solution, a set of 4 samples were prepared. The pH of these solutions were adjusted to values in the range of (2-5) using sulphuric acid. Samples of 100 ml of these solutions were mixed with 8g of adsorbent and shaken by mechanical stirrer (Fig.1) at 210 r.p.m for 90 minute. After the solution was separated from the solid adsorbent by filtration using Whatman-31filter paper. The filtrate was analyzed to determine the hexavalent chromium concentration in water after adsorption

The effect of adsorbent dose on hexavalent chromium removal was studied. Adsorption experiments with different amounts of adsorbent were conducted. 100 ml of hexavalent chromium stock solution with 88 mg/l concentration at best pH (which was 2)was shaken with adjusted amount of adsorbent at 210 r.p.m by mechanical stirrer for 90 minute, after that the solution was separated from solid adsorbent by filtration using Whatman31filter paper and the filtrate was analyzed by atomic absorption photometer.

To investigate the effect of mixing time, 6 samples with 100ml hexavalent chromium solution (88 mg/l concentration) were mixed with 8g of adsorbent at best pH (which was 2). The samples were shaken by using a mechanical stirrer at 210 r.p.m with stirring time (30, 60, 105, 150, 180 and 210) minute respectively. The solution was then separated from the solid adsorbent by filtration using Whatman-31filter paper and the filtrate was analyzed to determine the percentage of hexavalent chromium in solution after adsorption.

To study the effect of initial hexavalent chromium concentration on the removal efficiency, different concentrations of hexavalent chromium in water were studied at pH 2, stirring time of 90 minute and adsorbent dose of 8 gram in 100 ml of polluted water, the solution was then separated from the solid adsorbent by filtration using Whatman-31filter paper and the filtrate was analyzed to determine the percentage of *hexavalent chromium in solution after adsorption.*

Fig. (1) Laboratory adsorption unit (Jar Test).

Batch studies were adopted to obtain the equilibrium data. Different adsorbent weight (1, 2, 4, 6 and10) g respectively of waste tea leaves were added in 5 beakers containing 88 ppm Cr (VI) solution. The beakers were then placed on a Jar test and agitated continuously for a period of 180 minute which is enough to reach the equilibrium state (because the concentration did not change with time). Afterward the solution was filtered using Whatman-31filter paper. The filtrate was analyzed by atomic absorption spectrophotometer to estimate the equilibrium concentration.

The adsorption isotherm curves were obtained by plotting the weight of solute adsorbed per unit weight of adsorbent against the equilibrium concentration of boron in the solution.

$$qe = \frac{V_l(C_o - C_e)}{M}$$

Where:

qe =Adsorbent capacity (mg/g)

V_l =Volume of sample (l)

Co = initial concentration of hexavalent chromium in sample (mg/l)

Ce = Concentration of hexavalent chromium in sample after adsorption (mg/l) M = Mass of adsorbent (g)

The experimental data were compared using Langmuir, Freundlich Langmuir offered the following equation [14]:

$$qe = \frac{abC_e}{1 + aC_e} \quad (1)$$

Where

qe is the amount of adsorbate adsorbed per unit weight of adsorbent (mg/gm)

C_e is the equilibrium concentration of adsorbate in water (mg/l)

a and b are constants

Taking the reciprocal of both sides of the Langmuir equation yields:

$$\frac{1}{qe} = \frac{1}{b} + \frac{1}{abce} \quad (2)$$

Freundlich offered the following equation (Ruthven, 1984)

$$qe = Kf \cdot C_e^{\frac{1}{n}} \quad (3)$$

Where K_f and n are Freundlich adsorption isotherm constants.

Results and Discussion:

Effect of pH on Hexavalent Chromium Adsorption

Figure (2) shows the effect of solution pH on the removal of hexavalent chromium by adsorption onto waste tea leaves.

As the pH increased from 2 to 5 the adsorption of Cr (VI) decreased, increasing the pH from 2 to 3.5, the percent removal of Cr (VI) decreased from 91 to 59.6%, whereas as the pH increased from 3.5 to 5 the percentage removal decreased significantly from 59.6 to 54%.

At acidic pH, HCrO4-, Cr2O7-2and CrO4-2 is the predominant species of Cr (VI). It was observed that the maximum percentage of Cr (VI) removal was at pH 2. At pH 2 HCrO4- is the dominant species, at this pH the surface of the adsorbent is positive, this may lead the binding of negative charged HCrO4-, this species are most easily exchanged with OH- at the active surface [15, 16].

Under acidic conditions, the surface of the adsorbent becomes protonated and attracts anion species of Cr (VI). As the pH is increased above the zeta potential of the adsorbent, there is a reduction in the electrostatic attraction between the Cr (VI) and the adsorbent surface, with a consequent decrease in the adsorption percentage

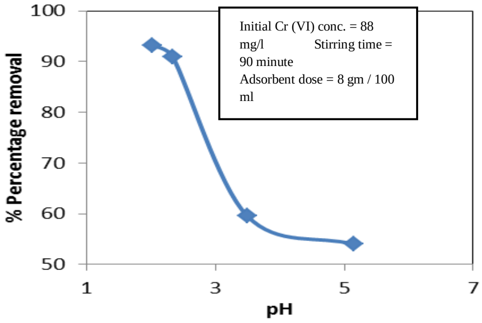

Fig. (2) Effect of pH on the percentage removal of hexavalent chromium

Effect of Mixing Time on Hexavalent Chromium Adsorption

Contact time is one of the effective factors in batch adsorption. The effect of contact time on the removal of hexavalent chromium by sorption onto waste tea leaves was shown in Figure (3). The importance of stirring lies in the fact that it maintains the adsorbent in suspension, offering the maximum surface and enough time to adsorbate adsorption. As observed in Figure (3) increasing contact time from 30 minute to 180 minute, increasing the percentage of Cr (VI) removal. Maximum Cr (VI) was observed within first 180 minute, and the time required to attain equilibrium was 180 minute.

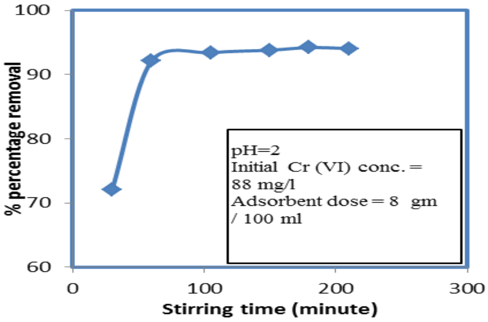

Fig. (3) Effect of mixing time on the percentage removal of hexavalent chromium

Effect of Hexavalent Chromium Concentration on the Percentage Removal

The effect of initial concentration of hexavalent chromium in water on the removal efficiency was presented in Figure (4).

As described from the figure, the hexavalent chromium removal efficiency decreased with the increase in initial chromium concentration. At higher concentration, the available sites of adsorption become fewer and hence the percentage removal of metal ions which depend upon the initial concentration decreases [15].

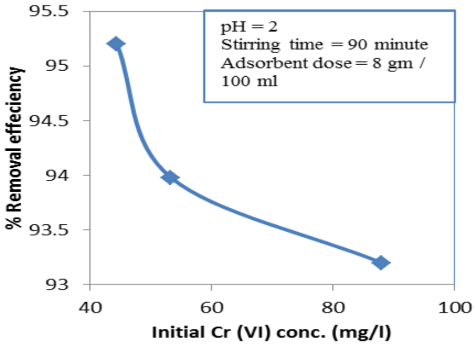

Fig. (4) Effect of hexavalent chromium concentration on the percentage removal Effect of adsorbent dose on the removal of hexavalent chromium from water

The effect of adsorbent dose on the adsorption of hexavalent chromium was presented in Figure (5). As illustrated from Figure (5), hexavalent chromium removal efficiency increased with increase in adsorbent dose due to the increase in number of adsorption sites, contact surface of adsorbent particles increased, and it would be adsorbed on adsorption sites and thus adsorption efficiency increased.

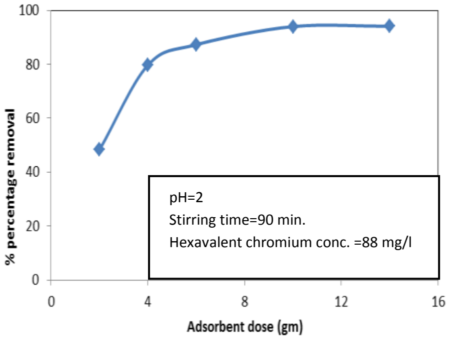

Fig. (5) Effect of adsorbent dose on the percentage removal of hexavalent chromium

Adsorption isotherm

Adsorption isotherm simplifies the relation between the concentration of the adsorbate and the hexavalent chromium concentration remaining in solution and also provides information on the mechanism of adsorption. The analysis of the isotherm data is important to develop an equation which accurately represents the results and could be used for design purposes. Data obtained from the equilibrium studies were used to fit curves for different adsorption models.

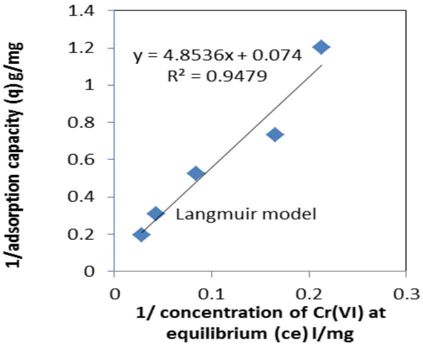

Fig. (6) Langmuir Isotherm adsorption model.

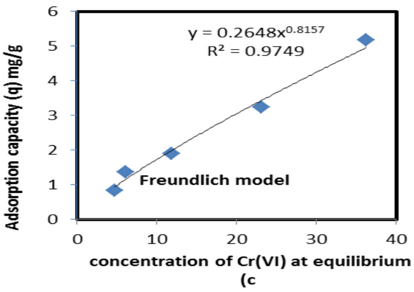

Fig. (7) Freundlich isotherm adsorption model.

Figures 6 and 7 illustrate the use of the Langmuir, Freundlich models for adsorption of hexavalent chromium at initial concentration of 88 mg / l, pH 2, stirring time 180 minutes and adsorbent dose from 1to 10 g per 100 ml.

Langmuir isotherm was achieved by plotting 1/Ce versus 1/qe (equation 2) to give a straight line with a correlation coefficient (R^2) equal to 0.947. The constant (a) which represents adsorption capacity, (b) which is related to the energy of adsorption were estimated from the slope and intercept of the linear plot

Freundlich isotherm was achieved by plotting Ce versus qe (equation 3) to give straight line with a correlation coefficient (R^2) equal to 0.974. The values of kf and n which were an indicative of adsorption capacity and intensity for adsorption were calculated from the slope and intercept of straight line.

From the values of correlation coefficient of the three models, Frundlich isotherm fit very well with the experimental data.

To test the applicability of the two models with experimental data, Figure 8 shows that Freundlich model was near to the experimental data rather than Langmuir model.

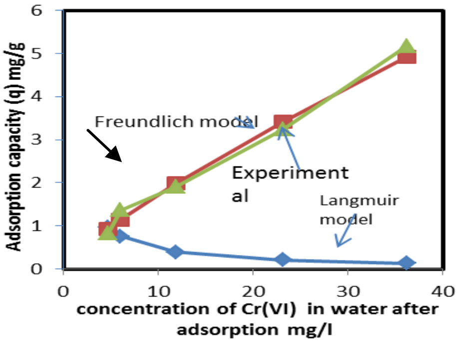

Fig. 8 Applicability of Langmuir and Freundlich models with experimental data

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استخدام مخلفات اوراق الشاي لتخفيض تركيز الكروم السداسي من المياه ا لعادمة الصناعية بالامتزاز

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الخلاصة:

تم اجراء هذا البحث لدراسة مدى تاثير الظروف التشغيلية على نسبة ازالة الكروم السداسي (مادة مسرطنة) من المياه العادمة الصناعية الخارجة من معمل الصناعات الكهربائية والتي تحتوي على تركيز من الكروم السداسي بقدر 88 ملغم /لتر باستخدام مخلفات اوراق الشاي كمادة ممتزة بعملية الامتزاز. تم تحضير ماء تخليقي يحتوي على تركيز من الكروم السداسي بقدر 88 ملغم/لتر. تم دراسة تاثير الدالة الحامضية، زمن الخلط، التركيز الابتدائي للكروم السداسي ونسبة مخلفات اوراق الشاي المضافة على نسبة الازالة للكروم اسداسي وكذلك دراسة ايزوثيرم الامتزاز. تم التوصل ان اعلى نسبة ازالة للكروم السداسي هي 94.26% باستخدام دالة حامضية 2، زمن خلط 180دقيقة وبكمية مضافة من مخلفات اوراق الشاي تقدر ب 8غم /100مللتر ماء ملوث، كذلك بينت النتائج ان الزمن اللازم للوصول الى حالة التوازن هو 180 دقيقة وان موديل فروندلج يتطابق مع النتائج العملية.