



Biosorption of chromium ions by using black tea leaves waste and the effect of some parameters on the removal of ions

Safaa Abdalrasool Ali

Institute of Genetic Engineering and Biotechnology for Postgraduate Studies, Baghdad University

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Abstract: Biosorption can be an effective technique for the treatment of heavy metals bearing waste water resulting from human and industrial activities. Several bioadsorbents have the ability to remove the heavy metals and thereby making water contaminant free. In the present study the biosorption of heavy metals using the black tea leaves waste and parameters affecting the biosorption of Cr ion; such as contact time, pH, temperature, dosage and particles size have been investigated. The present study showed that the contact time taken for maximum sorption of Cr ion was 120 min. The maximum percent removal of Cr ions on adsorbent was observed at pH 6 and significantly decreased by reducing the pH values and slightly decreased at higher pH values. The results indicated that the increasing of temperature from 35°C to 50°C induced that the adsorption capacity of Cr ions with highest adsorption capacity at 45°C and the concentration of 2 g was sufficient for maximum biosorption. It was obvious that the adsorption capacity of metal ion on tea waste increased by decreasing the particle size and the best particles size was 200 µm. The experiment results showed that maximum removal of Chromium ion by tea waste is 89.5 % at optimum condition.

Key words: Chromium ion, Biosorption, Tea waste.

)Safaamu2003@yahoo.com **Corresponding author:** should be addressed (Email:

الامتصاص الحيوي لأيونات الكروم باستخدام مخلفات أوراق الشاي الأسود وتأثير بعض العوامل على إزالة الأيون

صفاء عبد الرسول علي

معهد الهندسة الوراثية والتقنيات الاحيائية للدراسات العليا، جامعة بغداد

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الخلاصة: يعتبر الامتصاص الحيوي تقنية فعالة لمعالجة العناصر الثقيلة الناتجة من الفعاليات الصناعية والحيوية وهناك بعض المواد الحيوية ذات القابلية على ازالة هذه العناصر الثقيلة من المياه الملوثة. في هذه الدراسة تم استخدام مخلفات اوراق الشاي الاسود كمادة فعالة تستخدم للامتصاص الحيوي وتم دراسة بعض العوامل التي تؤثر على فعالية الامتصاص مثل زمن الاستيقاء، الرقم الهيدروجيني، درجة الحرارة، كمية المستخدمة، حجم الجزيئات. اظهرت الدراسة ان افضل زمن استيقاء هو 120 ثانية للحصول على افضل امتصاص حيوي وان افضل رقم هيدروجيني هو . انخفاض واضح للامتصاصية عند خفض الرقم الهيدروجيني بصورة اقل عند الرقم الهيدروجيني العالي وجدت النتائج ان رفع درجة الحرارة من 35 الى 50 سوف يؤدي الى زيادة قابلية الامتصاص الحيوي لأيونات الكروم، كانت الامتصاصية الحيوية 2غم في درجة حرارة 45 م°. من الواضح ان قابلية الامتصاصية للأيون تزداد بنقصان حجم الجزيئات وكانت افضل امتصاصية في حجم 200 مايكروميتر. اظهرت نتائج التجربة اعلى نسبة امتصاصية والتي بلغت 89.9% في الظروف المثلى.



Introduction

Rapid industrialization has led to increase disposal of heavy metals into the environment. The tremendous increase in use of heavy metals over the past few decades has inevitably resulted in an increased flux of metallic substances in the aquatic environment. The metals are of special concern because of their persistency. The metal ions i. e. Cd^{+2} , Zn^{+2} , Ni^{+2} and Pb^{+2} are important heavy metals in the soil water system since they are micronutrients in plants and animal. Mining activities, agricultural runoff, industrial and domestic effluents are mainly responsible for the increase of the metals released into the environment(1). All of the tea beverages, however, are obtained from the same basic tea leaves (*Camellia sinensis*) which, once the beverage has been brewed, become a waste that must be disposed of. Like other biomass residues, tea wastes represent an unused resource and pose increasing disposal problems (2). For these reasons, strategies are being investigated to evaluate their possible use as an energy source or in other value-added applications (3). The adsorption abilities of a number of low cost adsorbents (e.g., cheap zeolites, clay, coal fly ash, sewage sludge, agriculture waste and biomass) have been determined for the removal of heavy metals from water. Therefore, there is a need to look into alternatives to investigate a low-cost adsorbent which is effective and economic, for potential approach is the use of tea waste, Tea is one of the most popular beverages and about 3.5 million tons of tea was consumed annually in the world (4).

The aim of this study is to investigate the use of dried black tea leaves waste in the removal of heavy metals from aqueous solutions.

Materials and Methods

Bioadsorbent

10 g of tea leaves waste were purchased from Iraqi local market. The collected leaves were washed with distilled water, then the washed samples were drenched in 3M NaOH solution for 24 hrs. After 24 hours the drenched samples were washed with distilled water until the dye will remove. The washed samples were kept in hot air oven for overnight at 60 °C. Then the sample crushed with ball mill. The crushed samples were separated into different mesh size 52, 72, 100, 150, 200, 240 respectively using the sieve shaker.

Stock Solution Preparation

Different metal concentrations were prepared by dissolving potassium dichromate in double distilled water to get different metal concentrations. The metal solution was prepared in sterilized glassware. Prior to experiment all the glass were treated with 0.1 M HCL before and after the biosorption experiments to avoid binding of metals to it.

General Procedure for Optimization

Carry out batch adsorption for chromium concentration (50mg/l) with tea waste powder (0.5-3g) at pH (2-9) using series with Irlenmair flask (50ml), at temperature (30-60°C) and shaking different labeled flask (for 30-

120min). Finally the concentration of chromium ions were measured after adsorption by flame atomic spectrophotometric (Shimadzu AA-6200), calculated values of percentage removal.

Optimum Conditions

In order to obtain maximum removal of chromium ions optimum conditions have to be used. Such studies are described as follows: (5)

1-Effect of Contact Time: 50 mg/L of chromium solution (50mL) was added to (1g) of adsorbent into different labeled flask, at fixed pH 6 for all measurement. All flasks were kept at constant temperature 25°C for different times (30, 60, 90, 120, 150, 180min). After each agitation time, the content of each flask was then filtered, the equilibrium concentration of metal in each of the filtrate was determined by using Flame Atomic Adsorption Spectrophotometer to obtain the time at which removal of chromium ions accrue.

2-Effect of pH: Different solutions were prepared containing fixed amounts of chromium ions (50mg/l). The volume (50mL), adsorbent (1g) and time (90mins) were fixed with variable pH values (2, 3, 4, 5, 6, 7, 8, 9) using of waste solution of the metal which transferred into different 50 ml Erlenmeyer flask, corked and labeled. 1.0g each of the adsorbent was weighed into the different labeled flasks and in shaker for different pH (2-6) using 0.1N (HCl or NaOH) to adjust the pH. The concentration was determined after adsorption and the pH was obtained at which maximum adsorption occur.

3-Effect of Temperature: Same procedure maintained previously used (time, concentration of chromium, pH, and particle size), but with variable temperature (30, 35, 40, 45, 50, 55, 60 °C). The concentration of chromium ions was measured after adsorption in maximum temperature.

4-Effect of Adsorbent weight: Series of solutions containing fixed (time, temperature, pH, and particle size), with variable amounts of natural were prepared with modified adsorbent (0.5-3g). The concentration of chromium ions was measured after adsorption and in maximum adsorbent weight.

5-Effect of particle size: Different solutions containing fixed (time, temperature, pH, and weight of adsorbent) with variable of particle size of natural were obtained with modified adsorbent (200-700µm). The concentration of chromium ions after adsorption in maximum percentage removal was measured. The percent chromium removal efficiency was expressed as:

$$R\% = \frac{C_0 - C_f}{C_0} \times 100$$

where, C_0 and C_f are the initial and final concentrations of chromium (mg L⁻¹) in the aqueous solution (6).

Results and Discussion

The results for the effect of contact time on adsorption of Cr ions are shown in figure 1. It was observed that sorption percentage increased with the increase of time up to 120 min.

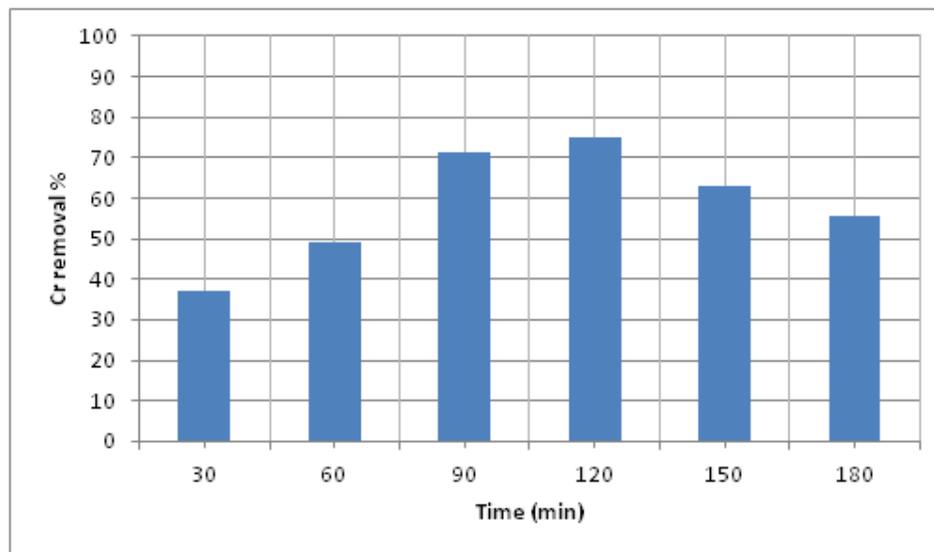


Figure 1: The effect of contact time on adsorption of Cr ions by tea leaves waste

The rapid initial rate increase followed by a slow rate at later period could be due to availability of excess adsorption sites on the adsorbent (7). The initial high adsorption rate might possibly be due to ion exchange followed by a slow chemical reaction of the metal ions with active groups on the sample (8).

In order to establish the effect of pH on adsorption of chromium ions a function of hydrogen ion concentration was determined and batch experiments were carried out at pH values 2-9. Figure 2 showed that the maximum percent removal of Cr ions on adsorbent was observed at pH 6 and significantly decreased by reducing the pH values and slightly decreased at higher pH values. At higher H^+ concentration the adsorbent surface becomes more positively charged hence reduces the

attraction between metal ions and adsorbent. Chromium adsorption was very low at $pH < 4$ and at $pH > 7$, metal removal was due to precipitation caused when OH^- ions formed complex with copper. The increase in metal removal as the pH increases can be explained on the basis of a decrease in competition between proton and metal cations for the same functional groups and by the decrease in positive surface charge, which results in a lower electrostatic repulsion between the surface and the metal ions. Decrease in adsorption at higher pH (above pH 6) is due to the formation of soluble hydroxy complexes (9).

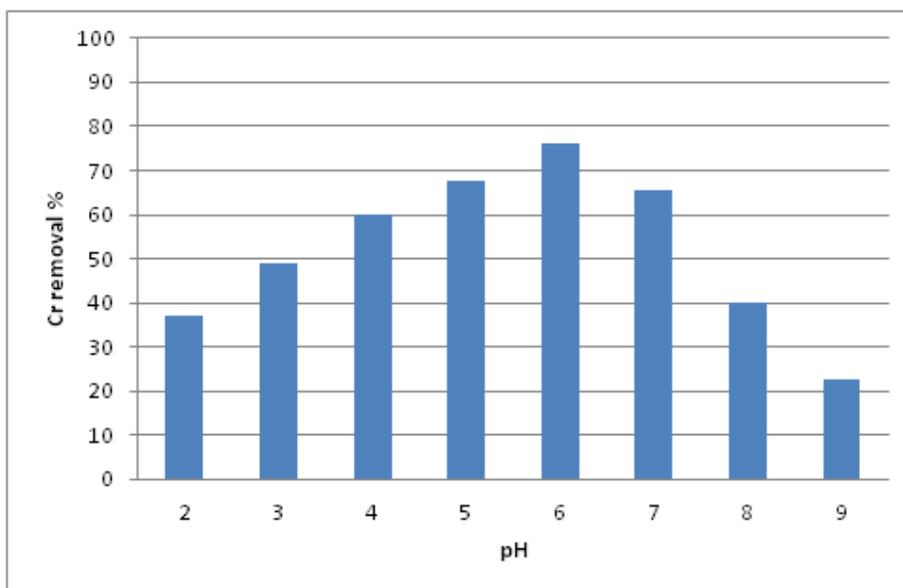


Figure 2:The effect of pH on adsorption of Cr ions by tea leaves waste

The effect of temperature on the Cr ions by tea leaves waste (figure 3), the results indicated that the increasing of temperature from 35°C to 50°C induced the adsorption capacity of Cr ions with highest adsorption capacity at 45°C. The effect of temperature on the adsorption of Ni(II) ions was presented by (10) for the adsorption of Ni onto tea factory waste indicated that increasing the temperature caused increasing the mobility of the metal cation. The increase of the adsorption yield and adsorption capacity at increased temperature indicated that the adsorption of nickel(II) ions by waste tea may involve not only physical but also chemical sorption. This effect may be due to the fact that at higher temperature an increase in active sites occurs due to bond rupture. The decrease in adsorption with increasing

temperature above 50°C, suggest weak adsorption interaction between biomass surface and the metal ion, which supports physisorption. According (11) the attractive forces between biomass surface and metal ions are weakened and the sorption decreases during temperature increasing.

Effect of the amount of adsorbent on metal adsorption was studied at fixed pH by various authors. The results of effect of adsorbent dose on the adsorption of chromium by tea leaves waste are summarized in figure 4. The results showed that the concentration of 2 g was sufficient for maximum biosorption. The percentage removal of heavy metal is seen to increase with adsorbent dose.

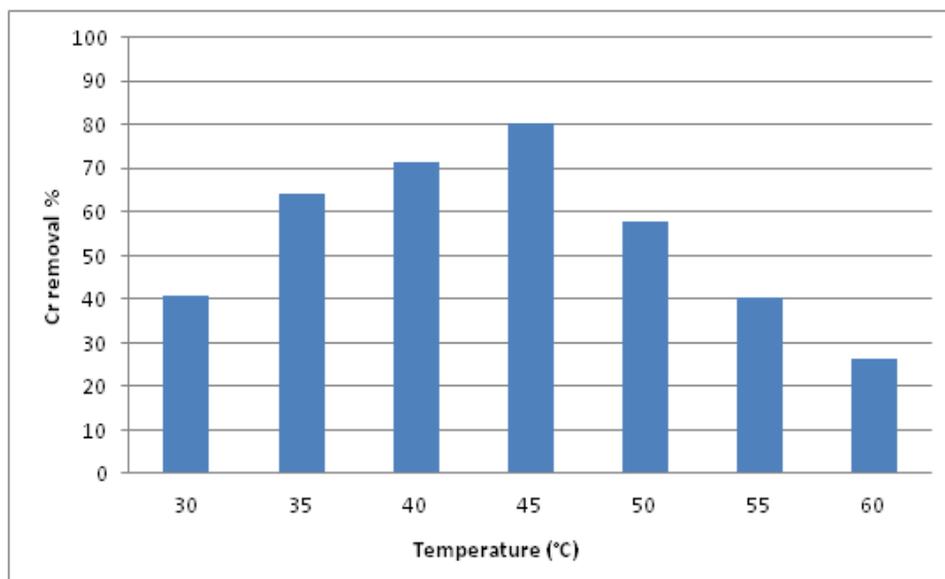


Figure 3: The effect of temperature on adsorption of Cr ions by tea leaves waste

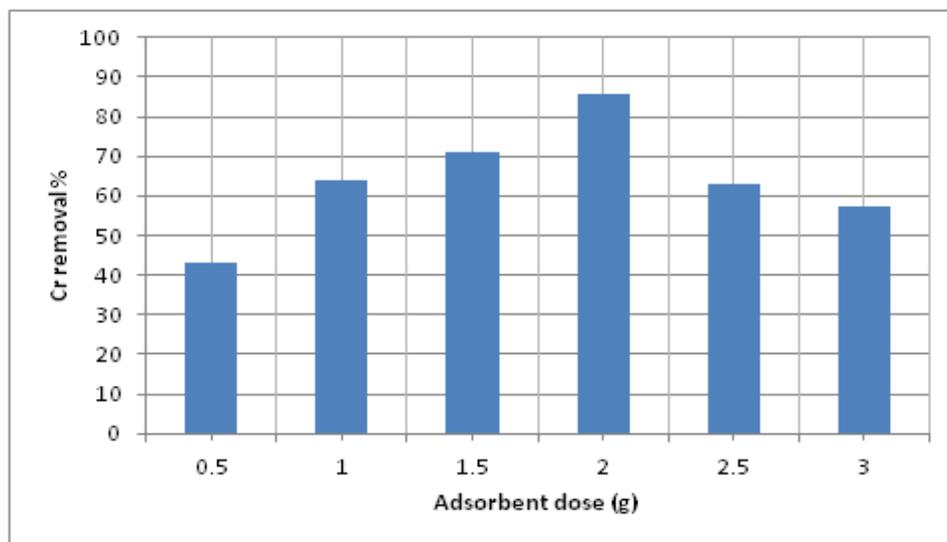


Figure 4: The effect of adsorbent dose on adsorption of Cr ions by tea leaves waste



The total amount of metal ions removed from the solutions increases by the amount of adsorbent. This is an expected result because as the adsorbent concentration increases, the number of adsorbent particles surrounding the metal ions or ratio of adsorbent particles to metal ions increases, therefore, these particles attach more ions to their surfaces. Increase in adsorption with adsorbent dose can be attributed to increased adsorbent surface area and availability of more adsorption sites. (12,13).

The average particle size was changed from 200 to 700 μm keeping the other variables set constant. The adsorption capacity of metal ion on tea

waste increased by decreasing the particle size (figure 5). This results can be attributed to the relationship between the effective specific area of the adsorbent particles and their sizes. This can be explained by the fact that for small particle a large external surface area results in a power driving force per unit surface area for mass transfer (14). The increase in the uptake by smaller particles was due to the greater accessibility to pores and to the greater surface area for bulk adsorption per unit mass of the adsorbent. Similar trend had been observed on removal of Cr(VI) by using *Pitchellobium dulce* Benth – A kinetic study (15).

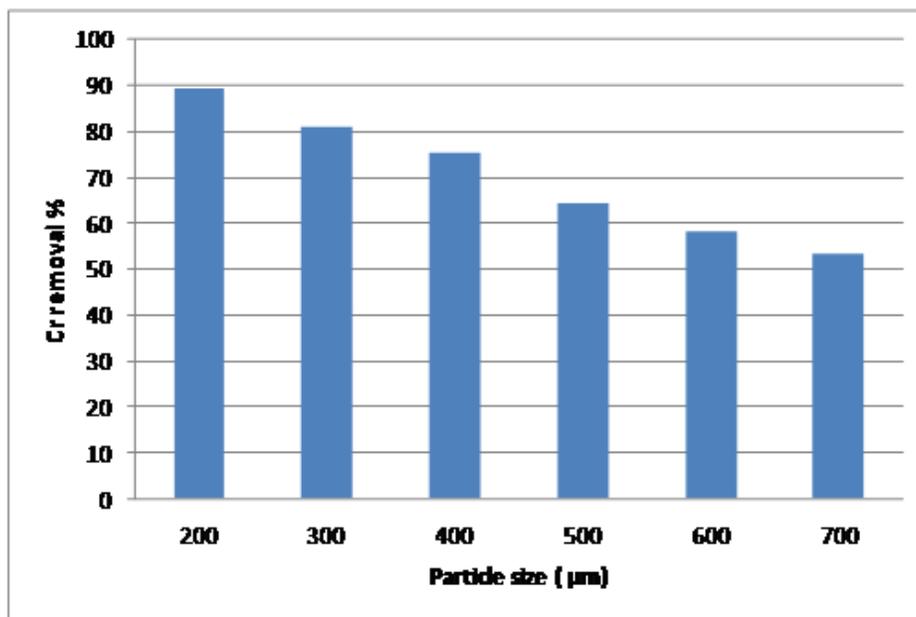


Figure 5: The effect of particle size on adsorption of Cr ions by tea leaves waste



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