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RESEARCH ARTICLE

REMOVAL OF HEXAVALENT CHROMIUM FROM AQUEOUS SOLUTION USING BITTER ORANGE POWDER

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ABSTRACT

Removal of chromium ions from aqueous solution using dried peel of bitter orange powder was performed through batch studies. Various process parameters like pH, contact time, biomass dose, and metal concentration were studied to investigate the optimum conditions for removal percent and the maximum removal capacity of Cr (VI). The chromium ions concentration was determined using UV-VIS spectroscopy. High removal percent was achieved at optimum parameters determined as follows: solid particle size= 75 μ m, contact time= 120 min, shaking rate= 250 rpm, pH= 1.2 and chromium concentration C_0 = 100 g/l. Around 94% of chromium ion was eliminated from aqueous solution with maximum removal capacity of 23.49mg/g at these conditions.

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INTRODUCTION

Nowadays, the contamination of water by toxic heavy metals through the discharge of industrial wastewater is a worldwide environmental problem. The term "heavy metal" refers to the metallic elements having density greater than or equal to 6.0 g.cm⁻³ (Barrera *et al.*, 2006). The most familiar metals are cadmium (8.65g/cm³), chromium (7.19 g/cm³), cobalt (13.53 g/cm³), nickel (8.91 g/cm³) and zinc (7.14 g/cm³). Among these toxic metals chromium has major impact on environment and it has both beneficial and detrimental properties (Sikaily *et al.*, 2007). In aqueous phase chromium mostly exists in two oxidation states such as trivalent chromium (i.e., Cr⁺³, Cr (OH)⁺² or Cr (OH)₂⁺, etc.) and hexavalent chromium (i.e., HCrO₄⁻, CrO₄²⁻ or Cr₂O₇²⁻, etc.). Most of the hexavalent compounds are toxic, carcinogenic and mutagenic and even it can cause lung cancer also (Li *et al.*, 2008). In recent years, contamination of the environment by Cr, especially hexavalent Cr, has become a major area of concern. Chromium is used on a large scale in many different industries, including metallurgical, electroplating, production of paints and pigments, tanning, wood preservation, Cr chemicals production, and pulp and paper production (Salunkhe *et al.*, 1998). Cr concentration ranging between 2000-5000 mg.L⁻¹ in the effluent compared to the recommended permissible limit of (2mg.L⁻¹) (Chandra *et al.*, 1997). In general, a wide range of

processes have been reported to eliminate the Cr(VI) from water and wastewater such as chemical precipitation, electrochemical reduction, sulphide precipitation, cementation, ion-exchange, reverse osmosis, electrodialysis, solvent extraction and evaporation, etc (Demiral *et al.*, 2008). The application of such methods is however cost intensive and is unaffordable for large scale treatment of wastewater. Hence, more economical means such as adsorption for the removal of toxic metals have been sought for. Therefore, there is a need to search an effective low cost adsorbent for economical wastewater treatment. A variety of natural plant biomass like green algae (Gupta *et al.*, 2001), rice brand (Singh *et al.*, 2005), tea waste (Malkoc *et al.*, 2005), olive bagasse (Demiral *et al.*, 2008) and hazelnut shell (Kobye *et al.*, 2004), etc. are used in the previous investigations. Literature survey reveals that the plant biomass is capable of reducing Cr (VI) to Cr (III) due to the active participation of its several anionic functional groups like hydroxyl, carbonyl, carboxyl, sulfhydryl and phosphoryl groups.

MATERIALS AND METHODS

Preparation of biosorbent

Peel of bitter orange were collected from Diyala city, washed many times with distilled water, dried at 120 C°, crushed, grounded by electrical grinder and sieved to both 75 μ m and 300 μ m. A part of dried peel of bitter orange was carbonized by a furnace at 250C° for 2h, then the prepared biosorbent used in batch experiments.

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Preparation of Cr (VI) solutions

A stock solution of Cr (VI) (1000 mg/L) was prepared by dissolving appropriate quantity of K₂Cr₂O₇ containing (1 gm) of Cr (VI) in (1L) deionized water. The stock solution was further diluted to desired concentration for obtaining the test solutions.

Batch Experiments

All experiments were carried at room temperature in conical flasks to investigate the influence of pH, contact time, biomass dose, and initial chromium concentration. Chromium solution was shaken with solid for desired contact time at a constant agitation speed 250 rpm and after filtration with filter paper, Cr (VI) ions concentration before and after run was analyzed by Using UV-Visible Spectroscopy type Jasco V-650 spectrophotometer. Metal removal percent was calculated using simple concentration difference method while the maximum removal capacity (q_m) was calculated depending on the following equation (Jimoh *et al.*, 2014):

$$q_m = \frac{C^o - C_e \times V}{m} \dots\dots\dots (1)$$

Where C^o and C_e are the initial and final chromium concentrations (ppm) at equilibrium respectively, V is the solution volume in (L), and m is the mass of the solid (gm).

RESULTS AND DISCUSSION

Effect of contact time (t)

The experimental runs measuring the effect of contact time on the batch removal of Cr (VI) at initial metal concentration 106 ppm in 25ml at pH=1.2 mixed with 0.1gm of 75µm dried powder indicated that increase in contact time from 15-120minutes enhanced the removal percent of Cr(VI) ions, As shown in Figure (1).

Effect of adsorbent dose

To study the effect of adsorbent dose (gm/L) on the uptake of Cr (VI), experiments were done with 25 ml of 100 mg/ L Cr (VI) at pH= 1.2, 2h at 250 rpm with 75µm dried biosorbent, while the amount of adsorbent added was varied from (0.05 - 03) gm. Results in Figure (2) show that the removal percentage of Cr (VI) from aqueous solutions increased with increasing the weight of biomass.

Effect of initial Chromium ions concentration (c_o)

The efficiency of chromium removal from aqueous solutions was investigated by changing the initial metal concentrations. These experiments were achieved with 25ml of different initial concentrations of metal ion ranging from (40-100) ppm at pH=1.2 and 0.1 gm of 75µm of dried biosorbent and 250rpm.

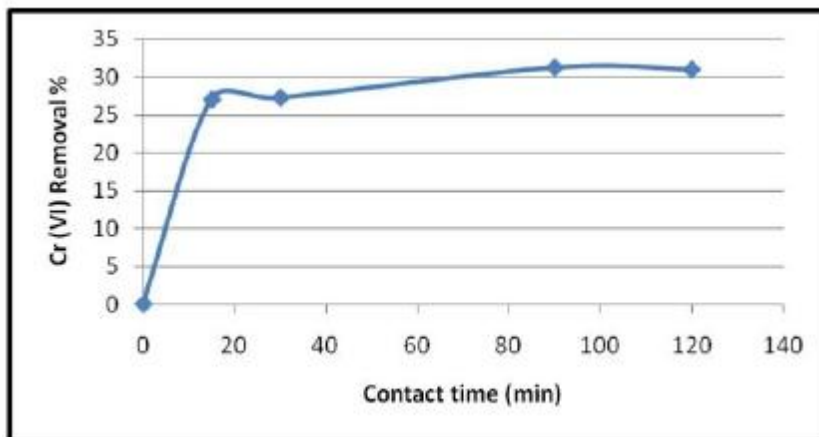


Fig.1. Effect of mixing time on removal of Cr (VI) from aqueous solutions C^o =106ppm, V=0.025L, pH=1.2, m=0.1gm (75µm)

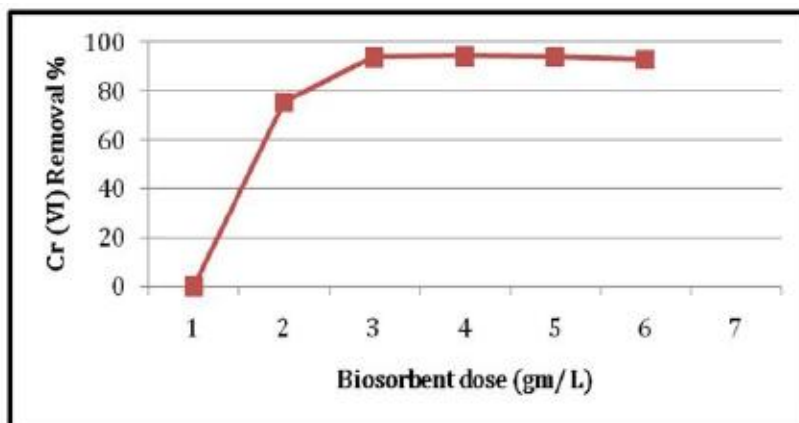


Fig.2. Effect of solid dosage on removal of Cr (VI) from aqueous solution c_o = 100 ppm, V=0.025 L, pH=1.2

The experiments data were measured at 120 minutes to make sure that full equilibrium was attained. As shown in Figure (3) the removal percent of Cr (VI) increased with increasing the initial ions concentrations.

of 25ml of $C_0=97\text{ppm}$, mixed with 0.1gm of $75\mu\text{m}$ of dried peel, 2h at 250 rpm were used. The optimum removal was obtained at $\text{pH}=1.2$.

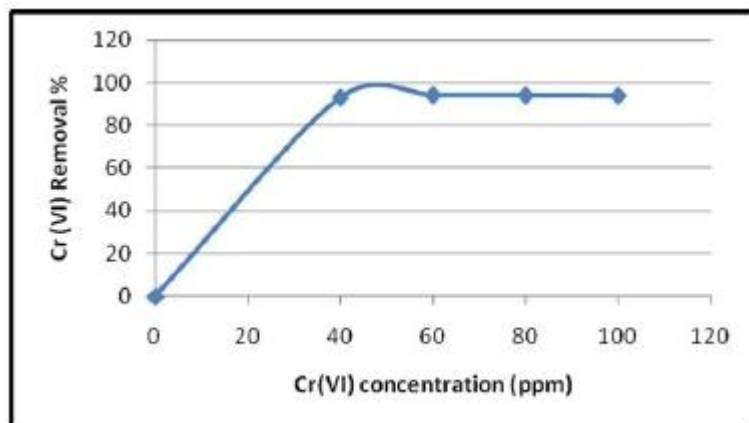


Fig.3. Effect of Cr (VI) concentration on its removal from aqueous solution $V=0.025\text{L}$, $t=120\text{min}$, $\text{pH}=1.2$, $m=0.1\text{gm}$ ($75\mu\text{m}$)

Effect of pH

Figure (4) shows the effect of pH on removal percentage of chromium ions in aqueous solutions. To investigate the influence of pH different values ranging (1.2, 2.0, 3.4, and 6.2) (neutral form) is the predominant species of Cr (VI). Hence, at pH 2.0 removal percent decreased due to the involvement of less number of HCrO_4^- anions on the positive surface. At higher pH due to more OH^- ions adsorbent surface carrying net negative charges, which tend to repulse the metal anions CrO_4^{2-} (Hadjmohammadi *et al.*, 2011) therefore, maximum removal of Cr (VI) from aqueous solution was achieved at pH 1.2.

At lower pH the surface area of the adsorbent was more protonated (due to more H^+ ions) and competitive negative ions adsorption occurred between positive surface and free chromate ions (HCrO_4^-). But in highly acidic medium ($\text{pH} \approx 2$) H_2CrO_4 removal percentages of Cr (VI) approximate in both size 75 and 300 μm . So these results prove that our biosorbent are efficient in uptake Cr (VI) in both sizes either burned or dried.

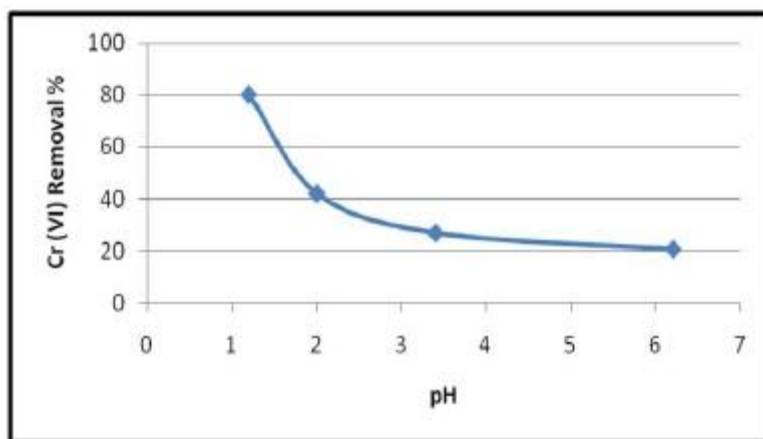


Fig.4. Effect of pH on removal of Cr (VI) from aqueous solution $C_0=97$, $V=0.025\text{L}$, $m=0.1\text{gm}$ ($75\mu\text{m}$)

Studying the effect of particle size, following experiments were done with 25ml of $C_0=101\text{mg/L}$ at $\text{pH}=1.2$, 2h at 250rpm, and 0.1gm of biosorbent using both 75 μm Burned peel and 300 μm dried and burned peel. Results in Table (1) show that the

To investigate the efficiency of chromium removal from aqueous solutions, several biosorbents from previous researches were compared with this work, as shown in Table (2) it can be considered that our solid powder is one of the best natural materials for isolate toxic chromium from aqueous solutions.

Table 1. Comparison percentage removal of Cr (VI) among dried and carbonized peel with different particle size

The biosorbent	Size of particles	Cr (VI) percent removal (%)
Dried peel of bitter orange	300 μm	95.46
Burned peel of bitter orange	75 μm	95.09
Burned peel of bitter orange	300 μm	94.49

Table 2. Comparison of Cr (IV) removal capacity between this study and others

Adsorbent	Removal capacity (q _m) mg/g	Reference
Fruit Shell of Gulmohar	12.28	Prasad <i>et al.</i> 2010
Pine Needles Powder	40.0	Hadjmohammadi <i>et al.</i> 2011
Natural Bentonite	12.65	Koyuncu <i>et al.</i> 2012
Saw Dust	20.70	Bhattacharya <i>et al.</i> 2008
Neem Bark	19.60	Bhattacharya <i>et al.</i> 2008
Fly Ash	23.86	Bhattacharya <i>et al.</i> 2008
Coconut Husk Fibres	29.00	Hamadi <i>et al.</i> 2001
Eucalyptus Bark	45.00	Sarine <i>et al.</i> 2006
Peel of Bitter Orange	23.49	This study

Conclusion

The present work shows that peel of bitter orange, is an efficient sorbent for removal of Cr (VI) ions from aqueous solution and it will be an alternative to more costly adsorbents. Experimental data indicated that the adsorption capacity was dependent of operating variables such as adsorbent dose, initial concentration of metal ions, pH and the contact time. The concluded optimum conditions from this study can be suggested as follows: chromium (VI) solution concentration=100 ppm, mixing time= 120 min, pH=1.2 and 0.1gm of dried biosorbent. According to these conditions, capacity established at this work was 23.49mg/g.

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