Iraqi National Journal of Chemistry

Journal homepage:
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Removal of Chromium Ions (VI) from Aqueous Solution by Utilizing Dried Tea Waste and Pomegranate Peel as Mixed Adsorbents

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Abstract

The present study was performed to evaluate the removal of chromium ions (VI) from aqueous solutions using dried tea waste and pomegranate peel as mixed adsorbent. Batch experiments were performed under various process parameters like pH, contact time, biomass dose, and initial chromium (VI) concentration to investigate the optimum conditions for removal percent and the maximam removal capacity of chromium ions (VI). High removal percent was achieved at optimum parameters determined as follows: pH= 1.4, contact time= 120min, shaking rate= 250 rpm, solid particles= 180μm, and chromium concentration= 20ppm. Around 88.1% of chromium ions (VI) was removed from aqueous solution with maximum removal capacity of q_m = 13.03 mg/g at these conditions.

Key Words: Chromium (VI), Mixed adsorbents, Heavy metals, adsorption, Batch experiments.

Introduction:

The United States environmental protection agency (USEPA) prepared a list known as the priority pollutants list in 1978 of 129 organic and inorganic pollutants found in wastewater. These pollutants constitute serious health and environment hazards; include the following thirteen metals antimony, arsenic, beryllium, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, thallium, and zinc. Heavy metals unlike organic compounds are non-biodegradable so, must be removed from wastewater. [1]

In aqueous solutions chromium exists in two oxidation states trivalent chromium and hexavalent chromium which its compounds more toxic than trivalent chromium. Hexavalent chromium compounds are toxic, carcinogenic, mutagenic, and cause lung cancer, while trivalent chromium is necessary for human nutrition and it is innocuous and immobile. Wastewater that produced during dyes and pigments production, film and photography, galvanometry, metal cleaning, plating and electroplating, leather and mining, cement, textile and steel fabrication industries, may contain elevated amounts of chromium ions (VI). [2,3]

The chromium concentration recommended by (USEPA) for potable water is 0.05mg/L and for irrigation water is 0.1mg/L according to the United Nations Food and Agricultural Organization. So, there is an urgent necessary to remove chromium (VI) from industrial wastewater before it can be discharged into environment. [4]

There are many processes have been reported to remove chromium ions (VI) from wastewater like ion-exchange, reverse osmosis, solvent extraction and evaporation, chemical precipitation, electrochemical reduction, sulphide precipitation, and cementation… etc.[5] However, these methods have disadvantage such as pollution, high cost, high energy input, and poor treatment efficiency at low metal concentration (less than 100ppm). So, it's important to search and develop efficient and economic metal removal process [6].

The purpose of this study was to evaluate the efficiency of dried tea waste and pomegranate peel as mixed absorbents and low priced method to remove chromium from aqueous solution.

Materials and Methods:

Preparation of biosorbent:

Tea waste and peels of pomegranate were collected from the local market in Diyala city. They washed many times with distilled water to eliminate dust and impurities, dried for a period of several days at room temperature. Both substances dried at 120C° for 6h, crushed, grounded with electrical grinder and sieved into 180μm. Finally, the resulting adsorbents dried tea waste (DTW) and dried pomegranate peels (DPP) were kept in containers to use them in batch experiments. Chemical or physical treatment to both of biosorbents was not used prior to experiments.

Preparation of Chromium ions (VI) solution:

A solution of hexavalent chromium was prepared by dissolving a calculated amount of potassium dichromate $K_2Cr_2O_7$ in distilled water to get a stock solution of (1000 mg/L). The stock solution was further diluted to the 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 JascoV-650 electrophotometer. The pH of each solution was adjusted by using the required amount of (0.1M) NaOH or (0.1M) H_3PO_4 before mixing the adsorbent. Metal removal percent was calculated using simple concentration difference method while the maximum removal capacity (qm) was calculated depending on the following equation [7]:

$q_m = C° - C_e \times V/ m$ ………. (1)

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

Result and Discussion:

Effect of adsorbent dose:

In order to study the effect of adsorbent dose on the uptake of chromium (VI), the experiments were done with 25 ml of 127ppm of Cr (VI) solution at pH= 5.2. The chromium ion solutions were mixed with different ratios of adsorbents with 180µm and shaked at 250rpm for 3h. It can be seen from table (1) that the best recovery of chromium (VI) obtained at the same ratios of adsorbents (DTW: DPP) (0.1: 0.1) gm which reaches to 92.0%. Biosorbent capacity (q) for this experiments calculated by applying equ.1 was 14.3mg Cr/g of dried adsorbents.

Table (1): Effect of the solid dosage on the removal of chromium (VI) from aqueous solution

	Tea waste gm	Pomegranate peel Gm	Percent Removal of Cr (VI) (%)
1	0.1	0.1	92
2	0.05	0.15	90.2
3	0.2	0	63.7
4	0.15	0.05	90
5	0	0.2	90

Effect of shaking time:

The influence of contact time on batch removal of Cr (VI) at initial metal concentration 127ppm in 25ml at pH= 5.2 mixed with (1:1) gm of 180µm (DTW: DPP). The solutions were shaken for (30, 60, 90, 120, and 150) min. at 250rpm. The results illustrated that the removal percent of Cr (VI) reached to the higher percent after few minutes. In this work at 30min the removal percent of chromium recorded 80% as shown in table (2).

Table (2): Effect of the mixing time on the removal of chromium (VI) from aqueous solution

	Time of mixing (min.)	Percent Removal of Cr (VI) (%)
1	30	80.0
2	60	77.5
3	90	78.4
4	120	79.4
5	150	79.0

Effect of initial chromium ions concentration:

In addition to adsorbent dose and shaking time, the initial concentration of chromium (VI) also investigated. Five different concentrations of Cr (VI) solution was treated with (0.1: 0.1) gm of adsorbents at pH= 5.2 for 3h. At the lowest initial concentration of Cr (VI) 20ppm gives the highest rate for the recovery of Cr (VI) with 82.1%. However, the results in table (3) reflect that the percentage of removal decreased with increasing the initial metal concentration. Earlier studies explained this behaviour due to those adsorbents has a limited number of active sites, which become saturated at a certain concentration [8].

Table (3): Effect of the initial concentration of Cr (VI) on the removal of chromium (VI) from aqueous solution

	Initial conc. Cr (VI) ppm	Percent Removal of Cr (VI) (%)
1	20	82.0
2	40	82
3	60	80.4
4	80	80.0
5	100	80.2

Effect of pH:

The effect of pH on metal adsorption is a very important parameter in batch adsorption studies. The functional groups in the adsorbents responsible for binding of metals ions in the adsorbent and the competition of metal ions that gets adsorbed to the active groups of adsorbents are affected by pH[9].

The influence of pH was studied by using 25ml of Cr (VI) with different values of pH ranging from 1.4, 2.2, 5.2, 8.2, and 10.4 mixed with (0.1: 0.1)gm of 180µm dried adsorbents for 3h at 250rpm. The practical measurements in table (4) show that the removal percentage of chromium (VI) from aqueous solution achieved under strongly acidic medium compared with the recovery percentage in the basic medium. The maximum adsorption value of Cr (VI) was 86.0% at pH= 1.4.

Hexavalent chromium exists as CrO_4^{-2}, $HCrO_4^{-}$, H_2CrO_4, and $Cr_2O_7^{-2}$ in the solutions. In low pH solutions, $HCrO^-_4$ is the widespread form hexavalent chromium which shifts to other forms like CrO_4^{-2} and $Cr_2O_7^{-2}$ as the pH increases. (14). At lower pH, the surface of the biomass protonated resultant from the presence of the carboxyl and amino groups, which leads to the strong attraction between Cr (VI) anions and the positive charges on the surface of the adsorbents. When, in the alkaline and neutral solutions the negative charges in the biosorbents repulse with negatively charged Cr (VI) anions [10]. So, the maximum removal efficiency of chromium ions was 86.1% and 86.0% at pH= 1.4 and 2.2 respectively. The minimum removal percent of Cr (VI) achieved at pH less than 2.2 as shown in table (4).

Table (4): Effect of pH on the removal of chromium (VI) from aqueous solution

	pH	Percent Removal of Cr (VI) (%)
1	1.4	86.1
2	2.2	86.0
3	5.2	83.3
4	8.2	54.4
5	11.2	48.6

To investigate the efficiency of chromium removal from aqueous solutions, many of biosorbents from previous researches were compared with this work, as shown in table (5) it can be concluded that the dried mixed adsorbents in this research is useful natural materials for isolate toxic chromium from aqueous solutions.

Table (5): Comparison of chromium ions (VI) removal capacity between this study and others

Adsorbent	Removal capacity (q_m) mg/g	Reference
Dried Bitter Orange Powder	23.49	11
Fruit Shell of Gulmohar	12.28	10
Saw Dust (Treated with formaldehyde)	3.6	12
Termenalia Arjuna Nut(treated with $ZnCl_2$)	28.43	13
Neem Bark	19.60	14
Fly Ash	23.86	14
DTW: DPP	13.4	This study

Conclusion:

This work show that the mixed adsorbents of dried tea waste and peel of pomegranate, is an efficient sorbents for removal of Cr (VI) ions from aqueous solution and it will be an alternative to more expensive adsorbents. Experimental data indicated that the adsorption capacity was relying on the 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=20 ppm, mixing time= 30 min, pH=1.4 and 2.2 and (0.1: 0.1) gm of DTW: DPP. Depending to these conditions, capacity established at this work was 13.03 mg/g.

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