

Removal of Hexavalent Chromium from Aqueous Solutions Using Azolla Plant Leaf

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Abstract

Soluble hexavalent chromium Cr is one of the most important and most dangerous toxic and carcinogenic heavy metals. This metal in accordance with health organizations has been classified as one of six probably carcinogenic agents through ingestion. This study was conducted to evaluate the level of removal of hexavalent chromium from aqueous solutions using Azolla plant leaf. In this experimental study, the effect of influencing variables was analyzed, including pH (2, 3, 5, 7, 8, 10 and 12), contact time (5 to 120 minutes), adsorbent dosage (0.1, 0.3, 0.5, 0.7, 0.9, 1 and 1.5 g/l) and initial phenol concentration (10-200 mg). Adsorption isotherms were studied using Langmuir, Freundlich and Temkin isotherms. The results showed that acid- heat- modified Azolla plant leaf had greater potential for absorption of chromium in comparison with washed with distilled water or unmodified conditions, so that the absorption rate was about 53% in pH 2 with an hour contact time. Also according to the results, the absorption rate in pH 2 was greater than in pH 4. Therefore, Azolla plant leaf compared with some adsorbents investigated so far is considered as an effective, suitable and inexpensive adsorbent for removal of Cr from aqueous solutions.

Keywords: *Hexavalent Chromium, Adsorption, Azolla, Aqueous Solutions, Adsorbent*

Introduction

Nowadays, health and environmental hazards resulting from heavy metals pollutions are among the most important

problems for human (1-3). Heavy metals enter the environment due to the

industrialization of societies and industrial activities, such as leather tanning, paints, fertilizers, mining, cement, photography, metal plating and textiles (4-6). These heavy metals are toxic inorganic contaminants that are not degradable, tend to accumulate in living organisms and cause severe health and environmental problems (7-10).

Among these, chromium is an odorless and tasteless heavy metal found naturally in rocks, plants, soil, volcanic dust, humans and animals. The most common forms of chromium in the environment are trivalent, hexavalent, and the metal (zero valent) form. Trivalent chromium exists naturally in many vegetables, fruits, meats, grains, and yeast. Hexavalent chromium and chromium in the metal form are generally produced via industrial processes. The main sources of chromium in drinking water are pulp mills, steel making, leather, wood preservatives, metal plating, and corrosion mineral deposits of chromium (III).

The chromium compounds have been released to the environment through leakage, poor storage or improper disposal.

The chromium compounds are very persistent in water as sediment (11, 12). Chromium is 500 times more toxic than chromium (III), more mobile in aquatic environments and is a strong oxidizing agent that can easily penetrate the skin. High levels of chromium have harmful effects on the lungs, stomach and intestines (13). Guidelines for Carcinogen Risk Assessment (U.S. EPA, 2005) reported chromium as a possible oral carcinogen to human. National toxicology program (NTP) in 2008 reported the carcinogenicity of chromium following chronic drinking water exposure in rats. In addition, evidence suggests that chromium causes mutation and DNA damage (14, 15).

International Agency for Research on Cancer (IARC) has classified chromium (4) in Group A (human carcinogen) and chromium (III) in Group 3 (non-carcinogen). Permissible level of chromium is 0.05 mg/l (50µg/l) of total chromium in drinking water (16). Therefore, the removal of chromium from water and wastewater is critical to protect the environment and health.

In addition, strict standards of wastewater discharge have led the industry to seek ways for wastewater treatment and chromium removal in permissible level. Various methods have been used so far to remove it, such as ion exchange, electrolysis, reverse osmosis and chemical and electrochemical precipitation (7, 17).

Some of these methods have no required efficacy for the removal of chromium, or require significant investment, high operating costs, disposal of remaining toxic sludge and expensive chemicals (18, 19). Adsorption is the most effective and least expensive method to remove chromium (4).

Activated carbon is also one of the important adsorbents for the removal of chromium but still expensive due to its high cost of production and poor selectivity. Therefore, it is important to produce a low-cost adsorbent with high efficiency and selectivity for the removal of chromium (19). Organic and inorganic substances have been employed as natural and modified adsorbents for treatment.

Clay minerals, among these, have been employed repeatedly to absorb pollutants due to low cost, high availability, high stability, ion exchange and adsorptive properties. However, clay minerals due to the negatively charged on the surface have little ability to absorb anionic pollutants such as nitrate, chromate, selenite and antimonite.

In addition to the inexpensive adsorbent, agricultural wastes such as eucalyptus charcoal (20), and peanut hulls (*Arachis hypogaea*) (21), as well as weeds like Russian knapweed flowers (22), have also been used to remove chromium. However, few studies have been reported to use leaves as adsorbent rather than bentonite. Some of them are mentioned below: Strawberry leaf powder for ammonium removal (23), Neem (*Azadirachta indica*) leaf powder as adsorbent for brilliant green (24), and lead (25), rubber leaf powder to absorb copper (26), *Imperata cylindrical* leaf powder to absorb nickel (27), and pineapple leaf powder as an adsorbent for methylene blue (28).

Satish et al. (2010) examined the mangrove leaf powder to remove hexavalent chromium from aqueous solutions. The results showed that this adsorbent has ability to absorb 60.24 mg/g according to Langmuir equation, and the maximum absorbance values was obtained in pH 2.

Thermodynamic studies indicated that absorption of chromium on this adsorbent is spontaneous in nature (4). Chen et al. investigated absorption of chromium (4) on the remnants of tobacco leaves in 2009. The results showed that the adsorption capacity was about 113.2 mg/g and absorption was influenced by pH; the maximum absorption was observed at pH 1; absorption of chromium on the surface of the adsorbent was fast and reached to equilibrium in by about 30 minute (29). Neem leaf powder after thermal treatment with hydrochloric acid was modified with 100 mmol/l copper solution and was used after drying as adsorbent of chromium (4).

A trace amount of the adsorbent (10 g/L) had ability to remove 99% of chromium in concentrations of 50mg/l (30). The absorption level of chromium on unmodified Neem leaves was lower (31). In addition, the the leaf powders of *Erythrina variegata var. orientalis* (32), *Syzygium cumini*, *Populus deltoids* (33), and *Euclea schimperi* (34), have been used to absorb chromium, but so far there has been no use of Azolla plant leaf as adsorbent. This study investigated the removal of Cr (4) from aqueous solutions using Azolla plant leaf.

Materials and Methods

Preparation of Adsorbent

Azolla dried leaves were collected in August 2014 from waste stabilization ponds in Kalat village, Gonabad, Iran. Weeds with the plant were separated carefully. The samples were washed several times with tap water to remove other pollutants such as dust, dried in the sun, grinded, graded by mesh 50 and stored in a glass container for later stages.

In addition to the powder prepared in the previous step, two modification methods were used to improve absorption: 1- Acid-heat treatment: 1 mM HCl was used in the

treatment that was heated on flame for about 1 hour and then was washed several times with distilled water up to disappearance of the final solution color. 2- Distilled water treatment: distilled water was used for this purpose and the adsorbent was washed several times with distilled water up to disappearance of the final solution color. Adsorbent precipitation and solution removal by pipette were applied to separate the adsorbent from the solutions. Finally, the adsorbents were poured on the filter paper and dried in the oven at 60°C for 24 hours.

Absorption Tests of Chromium

Chemicals used in this study were Merck, Germany. Potassium dichromate was applied to provide stock solution of Cr (4). All solutions for testing were prepared by diluting the stock solution. One gram of adsorbent was mixed with 50 ml solution containing 50 ppm chromium with certain pH.

For thorough mixing the solution with the adsorbent and achieving isothermal samples, refrigerated shaker (model JTS DL50) was used for one hour at ambient temperature at 150 rpm. The samples were centrifuged and the obtained solution was analyzed for chromium by atomic absorption instrument (Perkin Elmer, Model 700). Chromium levels were measured using standard methods for the examination of water and wastewater B3111 (35). All experiments were carried out with two replications along with control solution (adsorbent-free dissolved chromium), and the final concentration was measured with control solution. Absorption percentage was calculated by formula (1):

$$\% \text{ Adsorption} = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

Where, c_i : initial concentration of chromium (ppm), c_f : final concentration after adsorption (ppm). All containers used in the experiments were washed with 10% nitric acid and were then rinsed with distilled water several times.

Results and Discussion

As shown in Figure 1, the absorption level of chromium can be seen in acid-heat

treatment (rinsed leaf) of raw Leaf. The acidic treatment of leaf improves specific surface area of the adsorbent for absorption of chromium (30).

Plant cell walls composed of polysaccharides, lipids and proteins that have functional groups effective in absorbing metals, such as carboxyl, carbonyl, hydroxyl, amino, nitro aromatic, silicate and sulfonate (36).

Liu et al (2007) reported lower absorption of chromium on raw activated carbon compared to activated carbon treated with nitric acid.

When activated carbon is boiled with acid, Oxo-acid groups of COOH, OH and COOR will be formed that could be the reason for higher absorption of chromium by acidic treatment. Oxo-acid groups react with H^+ and form positive hydronium ions, such as $-COOH_2^+$, $-OH_2^+$ and $=CO=OH^+$ (37).

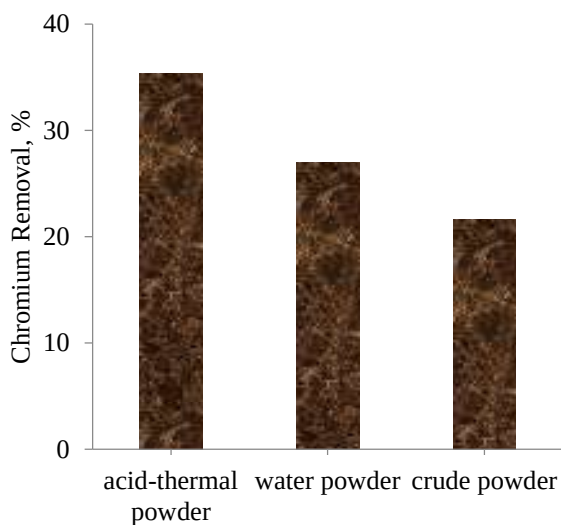


Fig 1: Absorption level in adsorbents modified by acid-heat, distilled water and raw water (100 ppm, pH 4, contact time of 1h)

The level of chromium (4) removal on different plant adsorbents are shown in Table 1. As it can be seen, the chromium absorption level by Azolla leaf powder is more rather than some plant samples. However, absorption level is higher in tobacco leaf that could be due to differences in the composition of the adsorbents. In addition to the parameters outlined in the table, other factors such as contact time, contact temperature and stirring intensity are also effective in the absorption rate.

Table 1: Comparison of chromium (4) adsorption levels in various plant adsorbents

Adsorbent	pH	Con (mg/l)	dosage (g/l)	Rem %	ref
Biomass MB1	5	50	10	14.97	(18)
MB2 biomass	5	50	10	19.87	(18)
Bagasse	5	50	10	9.65	(18)
Wheat Crust	5	50	10	13.32	(18)
The central pod corn *	5	50	10	10.88	(18)
Modified the tobacco leaves with water	5	50	10	42.7	(18)
Modified the tobacco leaves with acetone	5	50	10	25.2	(18)
Modified with ethanol	5	50	10	33.7	(18)
Tobacco leaves uncorrected	5	50	10	65.1	(18)
Euclea schimperi	5.6	20	20	93.9	(23)
Azolla leaf	4	100	20	38.17	
Azolla leaf	4	50	20	52.75	

Neurospora intermedia (MB1)

Neurospora sitophila (MB2)

* Corn cob grain

It should be noted that the chromium absorption level on the acid-heat adsorbent rose to 52.75 percent in pH 2. In fact, decrease in pH increased absorption rate. Kur et al. obtained similar results in 2013.

They studied the absorption of chromium (4) on leaf powders of *Syzygium cumini* and *Populus deltoids* after treating with acid-heat and observed good efficiency in pH 2 (33). Babu and Gupta (2008) examined the absorption of chromium (4) on the Neem leaf activated by acid-heat treatment and copper solution and reported 98% removal in pH 1-3 (30). Chromium (4) is in the form of $-HCrO_4$ at pH=2 that is the active form of chromium (4) to absorb; increase in pH converts $HCrO_4^-$

to CrO_4^{2-} (38). The decrease in absorption with increasing pH could be due to competition of chromium oxyanion and OH to access the absorption sites (34). Similar results were obtained for the absorption of chromium, on *Euclea chimperi* leaf (34), remnants of agricultural products (38), mangrove leaf powder (4), and plant biomass (39).

Conclusion

Investigation of Azolla plant leaf as an inexpensive and effective adsorbent to remove chromium indicated that negatively charged chromium species (chromate and dichromate) can be linked to positively functional groups on the adsorbent surface. Absorption rate is higher in low pH ranges because the surface functional groups are protonated in low pH ranges and can react easily with chromium anions. In addition, surface complexes can also be effective in removing chromium. This adsorbent is suitable for the removal of chromium from acidic solutions.

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