

Environmental Pollution Depletion of Chromium from Water Using Barberry Root

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Abstract. Heavy metals such as chromium from aqueous environmental contaminants are. In this study, the removal of Cr (VI) from aqueous solution using dried roots of Barberry under batch equilibrium experiments was investigated. The main process parameters were considered pH, initial Cr (VI) concentration, adsorbent weight, contact time and temperature. Cr (VI) was measured by Atomic Absorption. The result shows that the maximum removal of Cr (VI) was observed at pH 1.5. Also, by increase adsorption weight, the amount of adsorbed Cr (VI) on to adsorbent, increased to 92.26%. The amount of adsorbed Cr (VI) on to adsorbent, increased with an increase in the contact time but by increases initial concentration of Cr (VI), the amount of adsorbed Cr (VI) on to adsorbent, decreased to 85.44%. As well as the affinity of Cr (VI) towards the active sites of the adsorbent increases as temperature rises to 97.85%. The correlation coefficient for the Langmuir isotherm was significantly better than the Freundlich and the Temkin isotherm. Kinetics of adsorption was best fitted with the modified pseudo-first order kinetic model. These results demonstrate that roots of Barberry are effective and low-cost biomaterial for removal from aqueous solutions.

Keywords: Barberry roots, Cr (VI), Effluent, Heavy metals pollution, Natural adsorbent

1. Introduction

Chromium from the body through the gastrointestinal tract and are absorbed through the skin and into the body. The potential sources of Cr (VI) are various effluents from metallurgy, electroplating, leather tanning, textile dyeing, paint, ink, and aluminium manufacturing industries. These industrial effluents can contain Cr (VI), in the concentration range of 10 to 100 mg/L, which is much higher than the standard limit; 0.5 mg/L in industrial wastewater (EPA). In aqueous systems, chromium usually exists in both trivalent [Cr (III)] and Cr (VI) forms. Although Cr (III) is considered an essential trace element, Cr (VI) is toxic, carcinogenic, mutagenic and teratogenic [1]. Therefore, the removal of Cr (VI) from industrial wastewater is of particular concern. Advances in water and wastewater treatment technology need spur for the development of technologies that may be more effective and less costly. Nowadays, the contamination of water by toxic heavy metals through the discharge of industrial wastewater is a worldwide environmental problem that this pollution can also have a source of groundwater with the geological formation. The term "heavy metal" refers to the metallic elements having density greater than or equal to 6.0gcm^{-3} [2]. The most familiar metals are cadmium (8.65 g cm^{-3}), chromium (7.19 g cm^{-3}), cobalt (8.90 g cm^{-3}), copper (8.95 g cm^{-3}), lead (11.34 g cm^{-3}), mercury (13.53 g cm^{-3}), and nickel (8.91 g cm^{-3}) and zinc (7.14 g cm^{-3}). Among these toxic metals chromium has major impact on environment and it has both beneficial and detrimental properties. In aqueous phase chromium mostly exists in two oxidation states such as trivalent chromium (i.e., Cr^{3+} , $\text{Cr}(\text{OH})_2^+$ or $\text{Cr}(\text{OH})_2^+$, etc.) and Cr (VI) (i.e., HCrO_4^- , CrO_4^{2-} or $\text{Cr}_2\text{O}_7^{2-}$, etc.). Most of the Cr (VI) compounds are toxic, carcinogenic, and mutagenic and even it can cause lung cancer also.

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Cr (III) is essential for human nutrition (especially in glucose metabolism) and it is relatively innocuous and immobile. Therefore, the removal of Cr (VI) from industrial wastewater is of particular concern. Cr (VI) ions mostly exist as H_2CrO_4 form at high acidic medium ($pH \approx 1.0$). The maximum exit Cr (VI) concentration based on USEPA guidelines for potable water is 0.05 mg/l and the United Nations Food and Agricultural Organization recommended maximum level for irrigation waters is 0.1mg/l [3]. There are various methods for removing heavy metals including chemical precipitation, membrane filtration, ion exchange, liquid extraction or electro-dialysis [4]. However, these methods are not widely used due to their high cost and low feasibility for small-scale industries [5]. The widespread industrial use of low cost adsorbents for wastewater treatment is strongly recommended at present, due to their local availability, technical feasibility, engineering applicability and cost effectiveness [6], [7]. Most agriculture wastes or by products are considered to be low value products. As an alternative, a variety of inexpensive biomasses have been studied for their ability to remove Cr (VI) from aqueous solutions. Among these low cost adsorbents are microorganisms, seaweed, clay minerals, agricultural wastes, industrial wastes and various other low-cost materials [8]-[15].

The dynamics is an essential aspect of the adsorption process especially for practical applications. Therefore, the present investigation has been undertaken for studying the dynamic behavior of adsorption through batch experiments performed under different conditions of contact time, pH, adsorbent, initial concentration, particle size and temperature. A well-fitted kinetic equation was used to evaluate the suitable operational conditions for the removal process, and a Langmuir-type isotherm was modeled using kinetic data and experimental results.

2. Methods

2.1. Preparation of the soluble metal

The stock solutions of Cr (VI) (1000 mg/l) were prepared by dissolving $K_2Cr_2O_7$ (analytical reagent grade) in distilled water. The desired Cr (VI) concentrations were prepared from the stock solution by making fresh dilutions for each sorption experiment. The initial pH of the solution was adjusted by using a solution of HNO_3 or $NaOH$.

2.2. Preparation of adsorbent

Barberry roots were collected from South Khorasan, Birjand areas and soaked in distilled water for 24 hr before putting in an oven at 70 °C for 24 hours. Barberry roots using Mill Were powdered. Powders were sieved through a 100 μm mesh and were stored in a container away from moisture.

2.3. Batch adsorption experiments

Adsorption experiments were carried out in batch mode. In order to investigate the nature of Cr (VI), initially the effect of pH on percentage removal was carried out and then further experiments on the effect of contact time, adsorption weight, initial concentration and temperature were conducted by using optimized pH. Only one parameter was changed at a time while others were maintained constant.

In the first set of experiment, percentage adsorption was studied at various pH of (1.5–9) at constant adsorbent weight of 0.1 g/100 ml, initial Cr (VI) of 50 ppm and the predetermined time (10min) in a rotary shaker at a speed of 200rpm using series of 100 mL Erlenmeyer flasks.

Next second set of experiments were conducted with various contact time, initial Cr (VI) concentration (50ppm) at constant adsorbent weight (0.1 g/100 ml) and at optimized pH 1.5.

In the third set of experiment adsorption weight was varied (0.05–1 g/100 ml) while other parameters such as initial Cr (VI) concentration (50 mg/l), optimum time (90min) and optimum solution pH kept constant. In the fourth set of experiment Cr (VI) concentration was varied (25–200 ppm) and in the last set of experiment, temperature was varied at six different temperatures viz., 22, 25, 35, 40, 45 and 50 °C in a thermostat attached with a shaker. The constancy of the temperature was maintained with an accuracy of ± 0.5 °C. (22-50), and other optimum parameters kept constant. After completion of every set of experiments the supernatant was separated by filtration using Whatman filter paper and only 10ml of each sample was stored

for residual chromium analysis. The pH of each solution was adjusted using required quantity of HNO₃ or NaOH before mixing the adsorbent. Three replicates per sample were done and the average results are taken for calculation. The filtrate was analyzed using Atomic Absorption Spectrophotometer (AAS) (Shimadzu AA-6300; 228.63 nm). All the experiments were performed in.

The quantity of metal adsorbed at equilibrium was calculated by the following expression (Eq. 1):

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where m is the mass of adsorbent (gr), V is the volume of the solution (L), q_e is the metal quantity adsorbed at equilibrium (mg of Cr/mg of adsorbent) and C₀ and C_e is the initial and equilibrium concentrations of Cr (VI) ions (mg/L), respectively. For calculation of Cr (VI) removal percentage we used the following expression (Eq. 2):

$$R_e \% = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

3. Results and discussion

3.1. Effect of initial pH

Solution pH is one of the most important variables affecting the adsorption characteristics. The effect of pH on the removal of Cr (VI) by Barberrry roots was studied by changing the initial pH between 1.5 and 9. The relation between the initial pH of the solution and the percentage Cr (VI) removed is shown in Fig. 1. It is clear from Fig. 1 that there was a sharp decrease in the sorption capacity when pH was raised from 1.5 to 9 by adsorbent. The percentage removal of Cr (VI) decreased from 70.26% to 40% on increasing the initial pH from 1.5 to 9.

These results were considered since the dominant form of Cr (VI) is HCrO₄⁻ and the surface of the adsorbent is positively charged at low pH (pH = 1.5), but on increasing the pH, the HCrO₄⁻ species shifts to other forms; CrO₄²⁻ and Cr₂O₇²⁻. The decrease in the adsorption of Cr (VI) with increasing pH may have been due to the competition between the anions CrO₄²⁻ and OH⁻. Similar observations have also been reported by other research groups [16], [17]. Therefore pH=1.5 was considered as optimum condition. The maximum adsorption of Cr (VI) in the lower pH range has been observed by many authors [18]-[20].

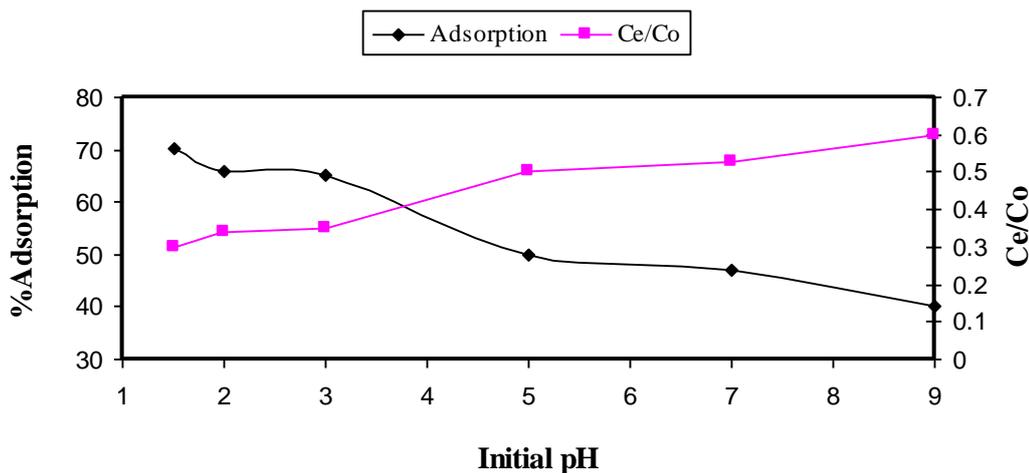


Fig. 1: Effect of pH on the adsorption of Cr (VI) ions by Barberrry roots (initial Cr (VI) concentration: 50 mg/L; mass of Barberrry roots: 0.1 gr; temperature: 22^oc; contact time of 10 min at mixing speed of 200 rpm).

3.2. Effect of contact time

The effect of contact time on the removal of Cr (VI) by Barberrry roots was studied by varying the contact time (10 to 180 min) for constant initial Cr (VI) concentrations. The relationship between the contact time and the percentage removal of Cr (VI) is shown in Fig. 2. The percentage removal of Cr (VI) increased

from 70.26 to 92.22% on increasing the contact time from 10 to 180 min for an initial Cr (VI) concentration of 50 mg/L. It was evident from Fig. 2 that the removal efficiency of Cr (VI) reached a maximum value in time 90 min and then no further significant increase was observed for contact time of up to 90 min, Therefore based on these results, a contact time of 90 min was selected in subsequent isotherm studies. This probably resulted from the saturation of the adsorbent surfaces with Cr (VI), followed by the adsorption and desorption processes that occur after saturation. The rate of adsorption was decreased during later stages of the Cr (VI) adsorption, probably due to the slow pore diffusion of the solute ions into the bulk of the adsorbent. Similar observations have also been reported in another investigation [21].

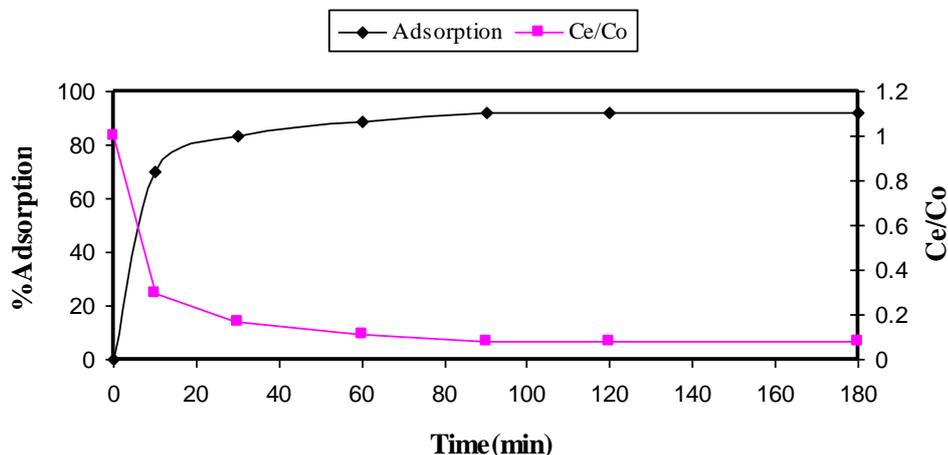


Fig. 2: Effect of contact time on the adsorption of Cr (VI) ions by Barberrry roots (initial Cr (VI) concentration: 50 mg/L; mass of Barberrry roots: 0.1 gr; pH 1.5 ; temperature: 22^oc at mixing speed of 200 rpm).

3.3. Effect of adsorbent weight

The effect of the adsorbent weight on the removal of Cr (VI) by Barberrry roots was studied by varying the adsorbent weight (0.05, 0.1, 0.2, 0.3, 0.5 and 1 g). The relationship between the adsorbent weight and the percentage removal of Cr (VI) is shown in Fig. 3.

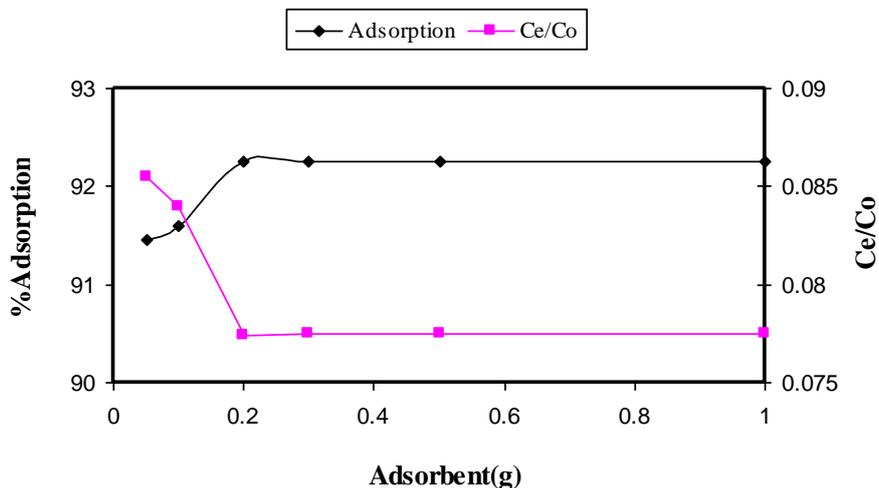


Fig. 3: Effect of adsorbent weight on the adsorption of Cr (VI) ions by Barberrry roots (initial Cr (VI) concentration: 50 mg/L; pH 1.5; temperature: 22^oc; contact time of 90 min at mixing speed of 200 rpm).

The percentage removal of Cr (VI) increased from 91.45 to 92.26% on increasing the adsorbent weight from 0.05 to 0.2 g. However, it is observed that after a weight of 0.2 g, there was no significant change in percentage adsorption of heavy metals. The increased Cr (VI) removal on increasing the amount of Barberrry roots was due to the increased surface area and adsorption sites available for adsorption. Similar observations have also been reported [22], [23].

3.4. Effect of concentration

The effect of initial Cr (VI) concentration on the adsorption of metal ions by Barberry roots was investigated with varying solution concentrations (25, 50, 100, 150, 200 mg/L) using 0.2 gr adsorbent weight at pH 1.5. The relationship between the initial Cr (VI) concentration of the solution and the percentage of Cr (VI) removed is shown in Fig. 4.

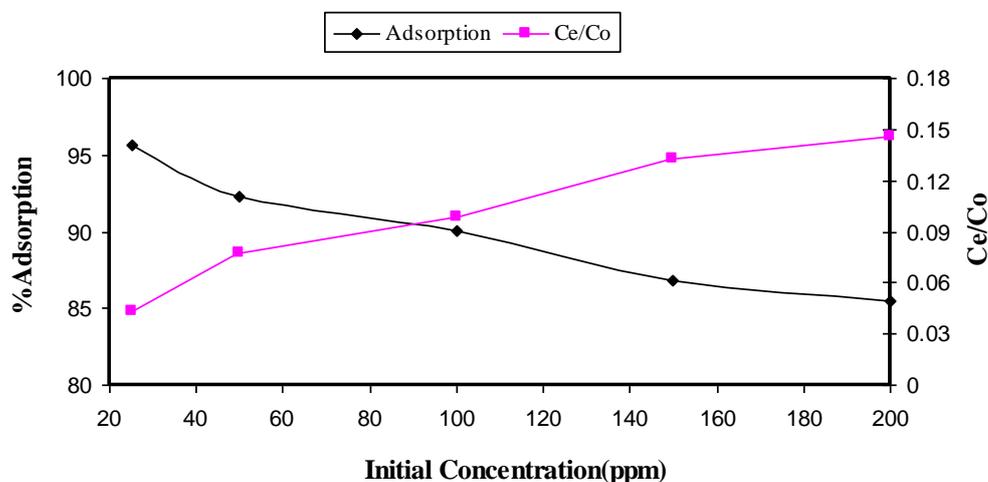


Fig. 4: Effect of initial concentration on the adsorption of Cr (VI) ions by Barberry roots (pH 1.5; mass of Barberry roots: 0.2g ; temperature: 22^oc; contact time of 90 min at mixing speed of 200 rpm).

Cr (VI) adsorption was significantly affected by the initial concentration of Cr (VI) in the aqueous solutions. The percentage of Cr (VI) removed decreased from 95.68 to 85.44% on increasing the initial Cr (VI) concentration from 25 to 200 mg/L. The decrease in the percentage removal can be explained by the fact the adsorbent had a limited number of active sites, which would have become saturated above a certain concentration.

3.5. Effect of temperature

Fig. 5 shows the effect of temperature on sorption on to natural bio sorbent under optimized conditions. It has been observed that sorption of Cr (VI) increases rapidly with increase in temperature from 22 to 50 °C. The percentage of Cr (VI) removed increased from 95.7 to 97.85% on increasing the temperature from 22 to 50 °C. The increase in sorption capacity of the bio sorbent is attributed to the enlargement of pore size and activation of the sorbent surface with rise in temperature. A further rise in temperature increases the mobility of the metal ions and reduces the swelling effect in bio sorbent, thus, enabling the metal ions to penetrate further [20], [24]. The results also indicate that the sorption of Cr (VI) on to natural fibers is an endothermic process.

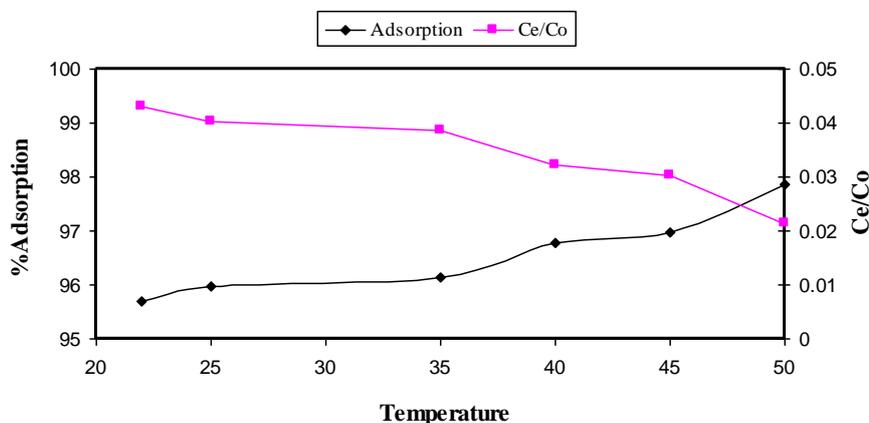


Fig. 5: Effect of temperature on the adsorption of Cr (VI) ions by Barberry roots (initial Cr (VI) concentration: 25 mg/L; mass of Barberry roots: 0.2 gr; pH 1.5; contact time of 90 min at mixing speed of 200 rpm).

3.6. Comparison with other adsorbents

The value of Q_{max} is of importance to identify which sorbent shows the highest adsorption capacity and is useful in scale-up considerations. The direct comparison of adsorbent capacity of walnut hull with other sorbents reported in the literature is difficult due to the varying experimental conditions employed in those studies; however, the walnut hull in this study possesses reasonable adsorption capacity in comparison with other sorbents (Table 1).

Table 1: Comparison of maximum adsorption capacity for Cr (VI) with various adsorbents.

Adsorbent	pH	Q_{max} (mg/g)	References
Sugar cane bagasse	2.0	13.4	[25]
Rice husk carbon	2.5	45.6	[25]
Pine needle	2.0	21.5	[26]
Almond	2.0	10.6	[26]
Aspergillus sp.	2.0	34.8	[27]
Barberry roots	1.5	20.41	This study

4. Conclusion

The result shows that the maximum removal of Cr (VI) was observed at pH 1.5. Also, by increase adsorption weight, the amount of adsorbed Cr (VI) on to adsorbent, increased to 92.26%. The amount of adsorbed Cr (VI) on to adsorbent, increased with an increase in the contact time but by increases initial concentration of Cr (VI), the amount of adsorbed Cr (VI) on to adsorbent, decreased to 85.44%. As well as the affinity of Cr (VI) towards the active sites of the adsorbent increases as temperature rises to 97.85%. These results demonstrate that roots of Barberry are effective and low-cost biomaterial for removal from aqueous solutions.

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