REMOVAL OF Cr(VI) FROM AQUEOUS MEDIUM BY CYNODON DACTYLON AND ORANGE PEEL POWDER

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ABSTRACT
Cynodondactylon and orange peel powder were investigated in this paper for the remediation of Cr(VI) from an aqueous medium at different pH values. The maximum adsorption capacities for Cr(VI) varied from 1.94 ppm to 0.03 ppm in the pH range of 2-4. The maximum percentage removal of Cr(VI) at pH 2 with orange peel powder and Cynodondactylon was 97.5 and 98.5 respectively. The effect of contact time and adsorbent doses were also studied. Experimental data revealed that the maximum percentage removal of Cr(VI) on treatment of 100 ml 2 ppm Cr(VI) solution with 1 g orange peel powder upto 3 hours was 97.5 %. The maximum percentage removal using Cynodondactylon with similar conditions is 98.5. Experimental data were the best fit in the Langmuir adsorption isotherm at 26°C and pH 6.5 for Cynodondactylon. This process of removal was considered due to the exploitation of abundant Cynodondactylon and orange peel.

Keywords: CynodonDactylon, OrangePeel Powder, Langmuir Adsorption, Phytoremediation, pH Value.

INTRODUCTION
Owing to non-biodegradability and accumulation in tissues leading to adverse health effects, hexavalent chromium has attracted the attention of researchers.¹,² Source of hexavalent chromium in water bodies is through industrial wastes, mining industries, and leather tanning operations.³,⁴ Chromium exists in 0, +3, and +6 oxidation states but Cr(III) is inactive on one hand and Cr(VI) is highly toxic on the other hand.⁵,⁶ Cr(VI) exists as HCrO₄⁻ at pH lower than 4 and as HCrO₄²⁻ and CrO₄²⁻ at pH greater than 4.⁷ Therefore adsorption of hexavalent chromium by orange peel powder and Cynodondactylon is pH dependent. The methods which are frequently employed for removal are ion exchange, electro dialysis, and reverse osmosis.⁸,⁹ These processes are not sustainable because of economic constraints. Adsorption by zeolites, coal fly ash,hydrated cement, and bentonites is also in practice¹⁰, in which active surface functional groups facilitate adsorption by a complex reaction between surface sites and adsorption.¹¹-¹⁴ In addition, activated carbon prepared from agriculture wastes e.g. coconut shell, Annona squamosa shell, risk husk maize stem, muskmelon peel, leaves of Ulmus carpinifolia and Fraxinus excelsior has been used for removal of heavy metals in general.¹⁵ The powdered leaves as well activated carbon have been utilized.¹⁶ A variety of aquatic plants have been found to be useful in removing Cr(VI) from an aqueous medium. Some of them worth mentioning are Hydrilla, Potamogeton,Spirallis, Lemna, Azolla, Eicchornea, and Trapa. These aquatic plants as well as medicinal plants have the capacity to remove one or more heavy metals from aqueous medium.¹⁷-¹⁹ The present study is to investigate the adsorption potential of orange peel powder for Cr(VI) removal at different pH values. Phytoremediation by Cynodondactylon, a perennial grass, have also been utilized for remediation of Cr(VI). Cynodondactylon removes Cr(VI) through its roots, stem and leaves whereas orange peel powder remediates Cr(VI) by surface functional groups. Vitamin C, cellulose and fibers are some of important constituents of orange peel powder. Pectin acts as an intercellular material. Effects of contact time and adsorbent doses have also been considered during experiment.

EXPERIMENTAL
Cynodondactylon has been collected from the field of the University Department of Chemistry. After repeated washing from double distilled water, moisture associated with Cynodondactylon is removed by Rasayan J. Chem., 15(4), 2450-2458(2022)
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filter paper and then made ready for use. Similarly, orange peel powder is collected after orange is used. It is washed with double distilled water and dried in the oven at 60°C. Dried orange peel is powdered to a homogeneous powder.

**Reagent and Solution**

100 ppm stock solution of Cr(VI) is prepared by dissolving an appropriate amount of K₂Cr₂O₇ in a one-liter measuring flask. 2 ppm and 4 ppm Cr(VI) solution are prepared by dilution of the stock solution. Cr(VI) gives a red violet color with diphenylcarbazide in an acidic medium which is measured at 540 nm. The reagent is prepared by dissolving 0.2 gm of diphenylcarbazide in 10 ml glacial acetic acid and now the solution is diluted to 100 ml with rectified spirit. The reagent has been supplied by Merck company known as Merckquant kit for the speedy test of Cr(VI) followed by reading in a U.V. double beam Spectrophotometer Pharo 300.

**Method**

Separate 250 ml conical flasks are taken to which 100 ml 2 ppm Cr(VI) solution are added. 10 gm Cynodondactylon is put into the solution in the conical flask for 1 day, 2 days, and 3 days at different pH values. pH values are adjusted by adding N/10 H₂SO₄ into the conical flask. The residual concentration is measured by U.V. double beam spectrophotometer. Again 1 gm homogeneous orange peel powder is added to conical flasks containing 100 ml 2 ppm Cr(VI) solutions. The mixture is agitated up to 1 hour, 2 hours, and 3 hours on a magnetic shaker. After filtration, residual concentrations in each flask are known. Now the same experiment is repeated with 1 g powder for 2 hours and 3 hours at pH 2 and pH 4.

**RESULTS AND DISCUSSION**

**Effect of Contact Time**

The treatment of the solution over a range of 1-3 hours in the case of orange peel powder and 1-3 days in the case of Cynodondactylon removed Cr(VI) up to 98.5% in 72 hours. The equilibrium concentration has been attained only in 48 hours. 1 gm orange peel powder when treated with 100 ml 2 ppm solution up to 3 hours, removal percentage is 97.5% and equilibrium concentration attained in 2 hours only. As the contact time increases, more surface area for adsorption becomes available to the adsorbate in the case of orange peel powder on one hand, and on the other Phyto remediation by Cynodondactylon becomes faster with increasing time.²⁰²¹ The increasing time enhanced the Cr(VI) removal both with Cynodondactylon and orange peel powder.

**Table-1: Residual Concentration of Cr(VI) ion after Treatment with CynodonDactylon up to Different Intervals of Time at 26°C and pH2**

| S.No. | Initial concentration | Mass of CynodonDactylon | Time  | Residual Concentration (Ct) | % Removal | qt | log qt | log Ct | Ct/qt |
|------|-----------------------|-------------------------|-------|-----------------------------|-----------|----|-------|-------|-------|
| 1    | 2 ppm                 | 10 gm                   | 24 hrs| 0.04                         | 98        | 0.0196 | -1.707 | -1.397 | 0.49  |
| 2    | 2 ppm                 | 10 gm                   | 48 hrs| 0.03                         | 98.5      | 0.0197 | -1.705 | -1.522 | 1.522 |
| 3    | 2 ppm                 | 10 gm                   | 72 hrs| 0.03                         | 98.5      | 0.0197 | -1.705 | -1.522 | 1.522 |

**Table-2: Residual Concentration of Cr(VI) ion after Treatment with CynodonDactylon up to Different Intervals of Time at pH 4**

| S.No. | Initial concentration | Mass of CynodonDactylon | Time  | Residual Concentration (Ct) | % Removal | qt | log qt | log Ct | Ct/qt |
|-------|-----------------------|-------------------------|-------|-----------------------------|-----------|----|-------|-------|-------|
| 1    | 2 ppm                 | 10 gm                   | 24 hrs| 0.28                         | 86        | 0.0172 | -1.764 | -0.552 | 16.29 |
| 2    | 2 ppm                 | 10 gm                   | 48 hrs| 0.27                         | 86.5      | 0.0173 | -1.761 | -0.568 | 15.606|
| 3    | 2 ppm                 | 10 gm                   | 72 hrs| 0.25                         | 87.5      | 0.0175 | -1.756 | -0.602 | 14.25 |
Table-3: Residual Concentration of Cr(VI) ion after Treatment with CynodonDactylon Upto Different Intervals of Time at 26°C and pH 6.5

| S.No. | Initial concentration | Mass of Cynodon | Time   | Residual Concentration (C_t) | % Removal | q_t  | log q_t | log C_t | C_i/q_t |
|-------|-----------------------|----------------|--------|-----------------------------|-----------|------|--------|--------|---------|
| 1     | 2 ppm                 | 10 gm          | 24 hrs | 0.28                        | 86        | 0.0172 | -1.764 | -0.552 | 16.27   |
| 2     | 2 ppm                 | 10 gm          | 48 hrs | 0.26                        | 87        | 0.0174 | -1.759 | -0.585 | 14.94   |
| 3     | 2 ppm                 | 10 gm          | 72 hrs | 0.25                        | 87.5      | 0.0175 | -1.756 | -0.602 | 14.25   |

Table-4: Residual Concentration of 100 ml 2ppm Cr(VI) ion after Treatment with Orange Peel up to Different Intervals of Time at 26°C and pH 2

| S.No. | Initial concentration | Mass of orange powder | Time   | Residual Concentration (C_t) | % Removal | q_t  | log q_t | log C_t | C_i/q_t |
|-------|-----------------------|-----------------------|--------|-----------------------------|-----------|------|--------|--------|---------|
| 1     | 2 ppm                 | 1 gm                  | 60 mins| 0.06                        | 97        | 0.194 | -0.712 | -1.22  | 0.309   |
| 2     | 2 ppm                 | 1 gm                  | 120 mins| 0.05                        | 97.5      | 0.95  | -0.709 | -1.3   | 0.026   |
| 3     | 2 ppm                 | 1 gm                  | 180 mins| 0.05                        | 97.5      | 0.95  | -0.709 | -1.3   | 0.0256  |

Table-5: Residual Concentration of 100 ml 2ppm Cr(VI) ion after Treatment with Orange Peel powder up to a different interval of Time at 26°C and pH 4

| S.No. | Initial concentration | Mass of orange powder | Time   | Residual Concentration (C_t) | % Removal | q_t  | log q_t | log C_t | C_i/q_t |
|-------|-----------------------|-----------------------|--------|-----------------------------|-----------|------|--------|--------|---------|
| 1     | 2 ppm                 | 1 gm                  | 60 mins| 0.79                        | 60.5      | 0.121 | -0.917 | -0.102 | 6.528   |
| 2     | 2 ppm                 | 1 gm                  | 120 mins| 0.78                        | 61        | 0.122 | -0.913 | -0.107 | 6.39    |
| 3     | 2 ppm                 | 1 gm                  | 180 mins| 0.78                        | 61        | 0.122 | -0.913 | -0.107 | 6.39    |

Table-6: Residual Concentration of 100 ml 2ppm Cr (VI) ion after Treatment with Orange Peel upto Different Intervals of Time at 26°C pH 6.5.

| S.No. | Initial concentration | Mass of orange powder | Time   | Residual Concentration (C_t) | % Removal | q_t  | log q_t | log C_t | C_i/q_t |
|-------|-----------------------|-----------------------|--------|-----------------------------|-----------|------|--------|--------|---------|
| 1     | 2 ppm                 | 1 gm                  | 60 mins| 0.8                         | 60        | 0.12  | -0.92  | -0.0969 | 6.66    |
| 2     | 2 ppm                 | 1 gm                  | 120 mins| 0.78                        | 61        | 0.122 | -0.913 | -0.107 | 6.39    |
| 3     | 2 ppm                 | 1 gm                  | 180 mins| 0.78                        | 61        | 0.122 | -0.913 | -0.107 | 6.39    |

Effect of pH
Among variables of temperature, concentration, time, and pH, pH is the important variable having a considerable effect on adsorption.22 Tables, Figures, and data analysis has made it very clear that adsorption of Cr(VI) both by Cynodon Dactylon and orange peel powder is maximum at pH 2. At pH 6.5 adsorption is lesser than at pH 2. Adsorption depends on the charge present at the surface of the adsorbent. If pH is lower than 4, Cr(VI) exists as HCrO$_4^-$ and CrO$_4^{2-}$ prominently and so adsorption of HCrO$_4^-$ takes place on the surface of the adsorbent at pH 2. In addition, phytoremediation by Cynodon Dactylon is maximum at pH 2. At pH 6.5 Cr(VI) is present in an aqueous medium as Cr$_2$O$_7^{2-}$. Adsorption compatibility of CrO$_4^{2-}$ and HCrO$_4^-$ is greater than OH$^-$ and so these ions have the potential to exchange with the OH$^-$ ions present in orange peel powder. Besides this, a complex reaction takes place at the surface between the sites of the surface and adsorbate. At lower pH, the neutral surface hydroxyl and carboxylic groups are active sites for adsorption but at higher pH, the functional group ionizes to give proton, and then it competes with the adsorption of HCrO$_4^-$. Thus adsorption of Cr(VI) at a high pH value is not facilitated. Adsorption of Cr(VI) onto orange peel powder may be described as:

$$S-OH^+ + HCrO_4^- \rightarrow S-HCrO_4 + H_2O \text{ at pH 2}$$

$$S-OH + CrO_4^{2-} \rightarrow S-CrO_4^- + OH^-$$
S-HCrO₄ and S-CrO₄⁻ correspond to the adduct formed due to adsorption.

Fig.-1: Percentage Removal of Cr(VI) Vs time with 10 gm of CynodonDactylon at 26°C and Different pH Values

Fig.-2: Percentage Removal of Cr(VI) Vs Time with 1 gm of an Orange Peel Powder at 26°C and Different pH Values

At pH 2 maximum removal efficiency is 98.5%. On one hand and on the other, removal efficiency is 87.5% at pH 4 and 6.5 by Cynodondactylon. Similarly, maximum removal efficiency by orange peel powder at pH 2 is 97.5% whereas removal efficiency at pH 6.5 is only 61%. The results have clearly indicated the marked increase of percentage removal with the change of pH from 6.5 to 2 by the mechanism described above.

**Adsorption Isotherm and FTIR**

Freundlich and Langmuir adsorption isotherm have been used for analyzing the experimental data. When log \( q_t \) versus log \( C_i \) is plotted, Freundlich adsorption isotherm is obtained. A plot of \( C_i \) Vs \( C_t \) gives

\[
q_t = \frac{(C_i - C_f)}{m \times V}
\]

Where, \( q_t \) is calculated as

Where \( m \) is the mass of adsorbent in g and \( V \) is the volume in liters.

The fitting graph indicates the applicability of both Freundlich and Langmuir adsorption isotherm. In case of Langmuir adsorption isotherm once HCrO₄ occupies a site, further adsorption is prohibited. All the sites in this model have been treated as equivalent in energy. But the possibility of some intra-particle diffusion cannot be ruled out. The diffusion of the adsorbate ions may take place into the fine pores of the adsorbent. Obviously, intra-particle diffusion may take place from the outer surface. Final linear portion of graphs shown may be due to intra particle diffusion. Fig.5 shows linearity in a plot of log \( q_t \) Vs log

logCᵢ and Fig.-4 and Fig.-6 shows linearity in a plot of \( \frac{C_i}{q_t} \) Vs Cᵢ.
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Fig.-3: Plot of log C<sub>t</sub> Vs Time at 26°C and pH 6.5

Fig.-4: C<sub>t</sub>/q<sub>t</sub> Vs C<sub>t</sub> (Langmuir Isotherm of Cr(VI)- CynodonDactylon System) at 26°C and pH 6.5

Fig.-5: log q<sub>t</sub> Vs log C<sub>t</sub> (Freundlich isotherm Cr(VI)- CynodonDactylon System) at 26°C and pH 6.5

Fig.- 6: C<sub>t</sub>/q<sub>t</sub> Vs C<sub>t</sub> (Langmuir Isotherm of Cr(VI)Ion- Orange Peel Powder System) at 26°C and pH6.5
The maximum % removal of Cr(VI) from aqueous medium using Cynodondactylon is 98.5% which is greater than 75.9% removed by activated fluorapatite. FTIR studies of orange peel powder before and after adsorption have been done with a view to know the adsorption. Peaks at 3600 cm⁻¹ shows the
presence of OH$^-$ groups and other peaks show the presence of unsaturated carboxylic acid and amines. FTIR peaks around 2921.6 cm$^{-1}$, 1731.64 cm$^{-1}$, and 1605.76 cm$^{-1}$ indicates NH stretching vibration, primary, tertiary alcohol groups. Ketone or aldehyde around 500 cm$^{-1}$ may be present.

The peaks at 1731.64 cm$^{-1}$ and 1371.96 cm$^{-1}$ before adsorption have shifted to 1605.76 cm$^{-1}$ and 1423.34 cm$^{-1}$ after adsorption the peaks at 769.89 cm$^{-1}$ and 2921.68 cm$^{-1}$ have disappeared and the peak at 518.86 cm$^{-1}$ has shifted to 425.86 cm$^{-1}$. That’s a certain type of peak for specific functional group disappears and new peaks appear due to linkage of the functional groups resulting from adsorption by orange peel powder. The shifts in peaks clearly indicate that adsorption has taken place on the surface of orange peel powder.

SEM$^{30-32}$ analysis before and after adsorption has been done to know the extent of adsorption on the active sites of the surface of the adsorbent. Figure 14-17 of SEM images clearly indicate that adsorption has taken place.
CONCLUSION

Cynodondactylon is an incessant weed and orange peel is also available in abundance. Orange peel and Cynodondactylon both are efficient for the removal of Cr(VI) at pH 2 upto 98.5%. A rapid biosorption takes place on the surface of Orange peel powder on one hand and on the other Cynodondactylon removes Cr(VI) by phytoremediation. Both Freundlich and Langmuir’s adsorption isotherms are applicable in the adsorption of Cr(VI). These adsorbents can be adopted on large scale too.
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