

# Removal of Hexavalent Chromium from Aqueous Solution using Chemically-Modified Sweet Lime (*Citrus limetta*) Peels

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**Abstract:** Chromium is an average toxic metal introduced into the ecosystem as a result of various industrial operations such as mining, smelting, surface finishing industry, energy and fuel production, fertilizer and pesticide, metallurgy, leather tanning, chromate preparation, etc. Chromium occurs in trivalent and hexavalent forms in aqueous solution/environment. Carcinogenic and mutagenic effects of Cr (VI) make it more toxic. Thus, biosorption of Cr (VI) ions from aqueous solution onto a low-cost adsorbent — *Citrus limetta* (Mousambi) peels — chemically modified peels (acid and alkaline treated peels) and raw peels were investigated to evaluate the batch parameters like effect of adsorbent dosage, initial chromium Cr(VI) ion concentration, contact time, pH and temperature. Greater percentage of metal Cr(VI) ion was removed with the increase in the amount of adsorbent used (Chemically modified and raw peels) and decrease in the initial concentration of Cr (VI) ion. The rate of adsorption is higher at a contact time of 96 h denoting the rate of uptake controlled by the rate at which the adsorbate is transported from exterior to the interior sites of biosorbent particles. Optimal pH value for Cr (VI) adsorption onto the chemically modified peels (alkaline and acid treated raw peels) was pH 10.0 and 2.0 for raw peels. Significant impact on biosorption of Cr (VI) ion was observed at a room temperature of 30–40°C. The comparative efficiency of alkaline, acid treated and raw peels of Musambi in removal of toxic Cr (VI) from its synthetic solution in batch modes were studied in the treatment of tannery effluent. The Change in lattice structure of adsorbent before and after adsorption was analyzed by FTIR and SEM analysis.

**Keywords:** Cr (VI); batch parameters; adsorption; calorimeter; Fourier transform infrared spectroscopy; high resolution-scanning electron microscope imaging.

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## 1. INTRODUCTION

Heavy metals are defined as metals with specific weight usually more than 5.0 g/cm<sup>3</sup> which is five times heavier than water. Thakur<sup>1</sup> classified heavy metals based on toxicity and classified chromium metal as metal with average toxicity. The toxicity of heavy metals occurs even in low concentrations of about 1.0–10 mg/L.

The average heavy metal, Chromium (Cr), is a steel-gray solid with a high melting point and an atomic weight of 51.996 g/mol. Chromium had oxidation states ranging from Cr (III) to Cr (+VI). Chromium forms a large number of compounds in both the Cr (III) and Cr (VI) forms. Chromium compounds are stable in the trivalent state and the hexavalent form being the second most stable state. The chromium (III) compounds are sparingly soluble in water and may be found in water bodies as soluble Cr (III) complexes, while the Cr (VI) compounds are readily soluble in water.

Chromium (III) is an essential element in humans with a daily intake of 50–200 µg/d recommended for adults. EPA has classified Cr (III) as a group D, not classifiable as to carcinogenicity in humans. Chromium III is much less toxic than Cr(VI). The respiratory tract is the major target organ for Cr(III) toxicity, similar to Cr(VI). Chromium (III) is an essential element in humans. Body can detoxify some amount of chromium (VI) to chromium (III). The respiratory tract is the major target organ for chromium (VI) toxicity, for acute (short-term) and chronic (long-term) inhalation exposures. Shortness of breath, coughing, and wheezing were reported from a case of acute exposure to chromium (VI), while perforations and ulcerations of the septum, effects have been noted from chronic exposure.<sup>2,3</sup> Human studies have clearly established that inhaled Cr (VI) is a human carcinogen, resulting in an increased risk of lung cancer.<sup>4</sup>

People who live in the vicinity of chromium waste disposal sites or chromium manufacturing and processing plants have greater probability of elevated chromium exposure than the general population. These exposures are generally to mixed chromium (VI) and chromium (III). Chronic exposure to high levels of Cr (VI) by inhalation or oral exposure may produce effects on the liver, kidney, gastrointestinal and immune systems, and possibly the blood. Dermal exposure to Cr (VI) may result in complications during pregnancy and childbirth. Most of the chromites mine discharge water contains 2–5 mg/L and chrome tanning effluent from tanning industries, other effluents from electroplating, mines etc. contain about 50–100 mg/L of Cr (VI), which is much higher than the permissible limit. Cr (VI) removal or reduction in industrial effluents is important before discharge into the aquatic environment. Compared to activated carbon, agricultural waste and industrial by-products may be cost-effective and have better sorbents, encouraging researchers to search for low-cost alternative sorbents.<sup>5</sup> Papaya woods, stem, rice bran, husk of Bengal gram, black gram, black tea leaves, wheat shell, cork biomass, rice husks, coconut coir pith, watermelon rind, etc. are used for Cr (VI) removal and reduction.

*Citrus limetta* fruit peels are the biosorbents used for hexavalent chromium removal from synthetic solution. The fruit peels were modified via chemical treatment for effective adsorption. A *C. limetta peel* which is commonly a waste is highly cost effective, has a possibility of metal recovery, there is no need for any additional nutrient requirement for metal recovery from synthetic waste / industrial effluent. Increased regeneration potential of biosorbent would alleviate the pressure concerning the supply of required amounts of new material. Development of effective biosorbents for adsorption of Cr (VI) depends on the type of pretreatment the peels are up to. The peels are pretreated by washing them with alkaline and acid solutions that is optimized for different batch modes of operation. Alkaline treated and acid treated peels are optimized at different adsorbent dosage, metal ion concentration, contact time, pH, and temperature and then characterized using FTIR, SEM and EDX imaging.

## 2. MATERIALS AND METHODS

### 2.1. Preparation of biosorbents:

#### 2.1.1. Preparation of raw peels:

Mousambi peels are collected from Mousambi fruits. The collected peels are kept drying for a three week period (shade drying). After drying, the next step was grinding and then screened. The grinded peels were passed through the sieves of size 4–5 mm. The peels are then stored in a glass tight bottle for further use.

#### 2.1.2. Preparation of chemically-modified peels:

- **Alkaline treated peels:**

The crushed Mousambi peel was treated with sodium hydroxide (NaOH) to improve the efficiency of metal uptake. In this study, 100 g of dried Mousambi peels biomass was treated with 1 L of (0.1 M) NaOH for 48 h in a shaker with constant shaking at 120 rpm. After repeated decantation and filtration, the chemically-modified biomass was washed with distilled water until the pH value of the solution was neutral. The modified peels were then oven dried at 80°C to constant mass, put in air tight bottle.

- **Acid treated peels:**

The sieved peels were treated separately with 0.4 mol/L nitric acid (HNO<sub>3</sub>) and distilled water. About 15 g of peels were soaked in 200 ml of 0.4 mol/L HNO<sub>3</sub> for 24 h in a shaker with constant shaking. They were filtered and rinsed with distilled water until the filtrate was near neutral.

### 2.2. Chemicals Required:

A stock synthetic standard solution of potassium dichromate was used to prepare the adsorbate solutions of required strength. Diphenyl carbazide, sulphuric acid, sodium hydroxide, nitric acid, acetone, potassium permanganate, hydrogen peroxide, chromium (III) nitrate non a hydrate, hydroxylamine were used.

#### 2.2.1. Preparation of chemical solutions:

- **Preparation of chromium (VI) stock solution:**

Stock solution (1000 mg/L) of chromium (VI) was prepared by dissolving potassium dichromate in distilled water. For biosorption experiments, Cr (VI) solutions (100 mg/L) were prepared from stock solution by dilution. Calibration standards 5, 10, 20, 50 and 100 mg/L were prepared.

- **Preparation of chromium (VI) standard solution:**

Standard Cr (VI) solution was prepared by dissolving 2.898 g of  $K_2Cr_2O_7$  in 1 L of distilled water, i.e., 0.2898 g of  $K_2Cr_2O_7$  dissolved and diluted to 100 ml with 2 N  $H_2SO_4$ . The solution is used for further experimental purposes.

- **Preparation of chromium (III) solution :**

Standard Cr (III) solution was prepared by dissolving 7.6960 g chromium (III) nitrate non a hydrate, i.e.,  $Cr(NO_3)_3 \cdot 9H_2O$  in 250 ml of distilled water and diluted to 1 L adding  $HNO_3$  to obtain a final concentration of 2% (v/v); 0.7696 g of  $Cr(NO_3)_3 \cdot 9H_2O$  was dissolved with 2 N  $HNO_3$  and diluted to 100 mL.<sup>6</sup> The solution is further used for other experimental purposes.

- **1,5 Diphenyl carbazide (DPC):**

0.25 g of 1,5 diphenyl carbazide (DPC) diluted in 100 ml of acetone (or) 250 mg of DPC in 80 ml of acetone. The solution is prepared freshly before use. Store in brown bottle for further use.

- **9 M Sulphuric acid:**

88 ml of  $H_2SO_4$  (98.08%) is diluted in 12 ml of distilled water.

- **0.1 M Sodium hydroxide solution:**

0.4 g of NaOH was diluted in 100 ml of distilled water.

- **0.4 M Nitric acid solution:**

2.5244 ml of  $HNO_3$  was diluted with 97.5 ml of distilled water. Store the solution in a brown bottle.

### 2.3. Apparatus:

Micropipette, conical flask, magnetic stirrer, volumetric flasks, blotting paper, Whatman filter no. 1, funnels.

### 2.4. Instruments:

Calorimeter, Fourier transform infrared instrument (FT-IR), high resolution scanning electron microscope imaging (HR-SEM).

## 3. PROCEDURE

### 3.1. Biosorption studies:

The biosorption capacity of Mousambi peels was determined by various concentrations (10–100 mg/L) of 100 ml of Cr solution with a particular concentration of Mousambi peels. The mixture was shaken in a rotary shaker at 120 rpm followed by filtration using Whatman filter paper (no. 1). The filtrate containing the residual concentration of Cr was determined spectrophotometrically at 540 nm after binding with 1, 5 DPC.

### 3.2. Determination of chromium:

In the determination of Cr concentration by UV–Visible spectrometric method, Cr (III) is converted to Cr (VI) using permanganate and 30% hydrogen peroxide. The Cr (III) is oxidized to  $(Cr_2O_7^-)$  dichromate with  $KMnO_4$  and determined calorimetrically using 0.25% 1,5 DPC to form a purple violet colored complex. The absorbance of the colored complex was measured using UV–Visible spectrophotometer at a wavelength of 540 nm.

### 3.3. Oxidation of Cr (III) to Cr (VI) and vice versa:

The sample solution containing 0.1–5  $\mu g$  chromium, 1 ml of 1 N  $H_2SO_4$  and 0.5 ml of 0.01 M  $KMnO_4$  were added and then the solution is warmed using boiling water for 40 min such that Cr (III) is oxidized to Cr (VI). The chromium concentration is then determined calorimetrically using 1, 5 DPC to form a purple violet colored complex. Using hydroxylamine Cr (VI) is oxidized to Cr (III).

### 3.4. Preparation for spectrometric analysis:

Under acidic conditions hexavalent chromium reacts with S-DPC to form a reddish violet colored complex resulting from the reaction of hexavalent Cr with S-DPC. The chromate oxidizes DPC to DPCO (diphenylcarbazone). The determination of Cr with derivatizing agent DPC, enables the separation of Cr without a previous separation step, because the reaction is selective for Cr (VI). The absorbance of colored complex was measured spectrometrically at 540 nm.<sup>7</sup> Acid solutions of potassium dichromate are colored and intensity of this color is proportional to the concentration of the dichromate anion

in solution. For the purpose of comparison, the absorbance of Cr (VI) in the unknown acidified sample solution was measured at 440 nm in the absence of chromophoric reagent.

### 3.5. Estimation of standard calibration curve:

K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> standard solution of 0, 20, 50, 100 mg/L were prepared by pipetting 0, 2, 5, 10 ml of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> stock solution in four different 100 ml volumetric flasks. To each of the volumetric flasks, 3 ml of 9 M sulphuric acid solution (50% v/v) was added and diluted to 100 ml with distilled water. To each four test tubes containing 10 ml of four standard solutions, 0.5 ml of S-DPC was added. Appearance of pink (dark) color indicates the presence of chromium metal. Absorbance was read at 540 nm. The absorbance reading of the standard solutions was used to construct a calibration curve

## 4. BATCH EQUILIBRIUM STUDIES

A total of 50 ml of Cr (VI) solution (100 mg/L) at the controlled pH was taken in a 250 ml conical flask with a fixed dosage of sorbent. The mixture was agitated on a shaker at a speed of 120 rpm at room temperature for a time period which was sufficient for the chromium uptake process to reach equilibrium.

### 4.1. Batch studies:

#### 4.1.1. Different concentrations of sodium hydroxide:

Sodium hydroxide is used in alkaline treatment of *Citrus limetta* sieved peels. Different concentrations of sodium hydroxide is mixed with roughly 0.75 g of sieved peels and kept soaked for 24 h in a shaker with shaking at 120 rpm. They were filtered and rinsed with distilled water until the filtrate was near neutral. This is done in order to increase the efficiency of adsorption of metal waste. Different concentrations of NaOH (0.005, 0.01, 0.05, 0.1, 0.3 and 0.5 M) were dissolved in water containing 0.01 g of chromium (Cr (VI)) solution and then 0.05 g of biosorbent was added on it and incubated at different time periods (24, 48, and so on till 120 h). The samples were filtered and then analyzed calorimetrically at 540 nm using DPC.

#### 4.1.2. Effect of adsorbent dose:

The effect of adsorbent dose for the removal of Cr (VI) from aqueous solution was found out. The adsorption study was carried out at an initial Cr (VI) concentration of 0.75 g/100 ml with different adsorbent doses (0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 5.0, 7.5, 8.0 g/L). The results were obtained at different time intervals from 24–120 h. At the end of each interval, the sample is filtered and observed calorimetrically at 540 nm using DPC.

#### 4.1.3. Effect of different metal concentrations:

The effect of varying metal (Cr (VI)) concentration was studied. Varying chromium concentration, i.e., 25, 50, 75, 100 mg were dissolved in 100 ml of water, 0.75 g of biosorbent was added and mixed well. The sample was placed in shaking condition for different time intervals such as 24, 48, 72, 96 and 120 h, respectively, at room temperature. At the end of the time intervals, the samples were filtered and observed calorimetrically at 540 nm using DPC. Similar results were obtained by Namashivayam and Kumar.

#### 4.1.4. Effect of contact time in Cr (VI) uptake:

The time required for biosorption of Cr (VI) on 0.75 g/100 ml raw and chemically-modified sweet lime peels were studied. The adsorption of Cr (VI) was studied at different time intervals such as 24, 48, 72, 96, 120 h, respectively. To the sample obtained from different time intervals 0.5 ml of DPC was added and observed calorimetrically at 540 nm.

#### 4.1.5. Effect of pH in Cr (VI) uptake:

The effect of pH on Cr (VI) uptake using raw and chemically-modified sweet lime peels were studied calorimetrically. Cr (VI) adsorption was studied at varying pH (2, 4, 6, 8, 12), respectively. To the above sample 0.5 ml of DPC was added and observed at 540 nm calorimetrically.

#### 4.1.6. Effect of temperature in Cr (VI) uptake:

Temperature is another major factor affecting Cr (VI) adsorption. Temperature has an influence on biosorption or not is identified by maintaining it in different ranges such as 10–20°C, 20–30°C, 30–40°C, 40–50°C and 50–60°C, respectively. To the above sample 0.5 ml of DPC was added and observed at 540 nm calorimetrically.

4.2. Characterization of biosorbents:

4.2.1. FT-IR studies:

FT-IR studies were used to identify the functional groups present in fruit/citrus peels. The samples were examined by PERKIN ELMER SYSTEM ONE FT-IR/ATR within the range of 450–4000 cm<sup>-1</sup>. KBr was used as background material in all analysis. Fruit peel powder was mixed with KBr in 1:100 mg ratio and pressed to form pellet. (Solid samples are dispersed in KBr or polyethylene pellets depending on the region of interest). FT-IR spectra of fruit peels indicated the presence of —CO, —OH, —NH<sub>2</sub>, —CN, —CH, etc. which are important sorption sites.

4.2.2. HR-SEM studies:

The Quanta 200 FEG scanning electron microscope is a versatile HR-SEM for analyzing the surface morphology of sample. Non-conducting samples are coated with a thin layer carbon or gold. Energy dispersive X-ray spectroscopy (EDX/EDS) is an analytical capability where element specific radiation is used for chemical characterization of the surface near volume.

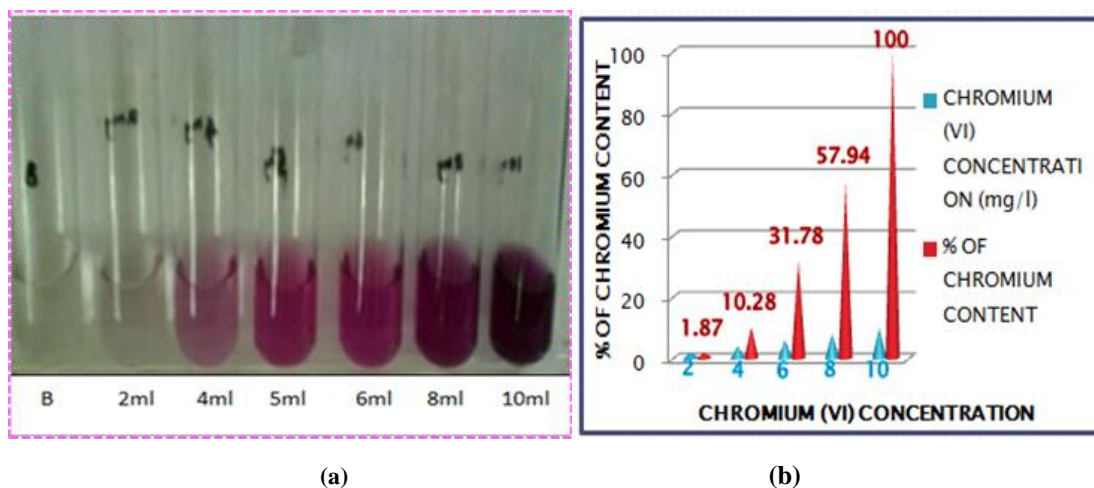
5. RESULTS AND DISCUSSION

5.1. Cr (VI) standard calibration curve:

This procedure measures only hexavalent chromium (Cr<sup>6+</sup>). Therefore to determine total Cr convert all the Cr to hexavalent state by oxidation with KMnO<sub>4</sub>. The hexavalent chromium is determined calorimetrically by reaction with DPC in acid solution. A red-violet colored complex of unknown composition is produced. (The reaction is very sensitive, the molar absorptivity based on chromium being about 40,000 Lg<sup>-1</sup>cm<sup>-1</sup> at 540 nm.) To determine total chromium, the sample is digested with H<sub>2</sub>SO<sub>4</sub> mixture and oxidized with KMnO<sub>4</sub> before reaction with DPC.

| PARTICULARS                            | BLANK | PREPARATION OF STANDARD SOLUTIONS |    |    |    |    |
|--|-------|-----------------------------------|----|----|----|----|
|  |       | S1                                | S2 | S3 | S4 | S5 |
| Chromium (VI) concentration (mg/ml)    | 0     | 2                                 | 4  | 6  | 8  | 10 |
| Volume of chromium Concentration (ml)  | 0     | 2                                 | 4  | 6  | 8  | 10 |
| Volume of 9M Sulphuric acid (ml)       | 3     | 3                                 | 3  | 3  | 3  | 3  |
| MAKE IT TO 100ml USING DISTILLED WATER |       |                                   |    |    |    |    |

Different concentrations of Cr (VI) solutions were prepared and optical density of the solutions were found using DPC solution. The appearance of purple or pink color denotes the presence of chromium in solution (Fig. 1).



| PARTICULARS                       | BLANK | T1   | T2    | T3    | T4    | T5   |
|-----------------------------------|-------|------|-------|-------|-------|------|
| Volume of chromium solution (ml)  | 0     | 10   | 10    | 10    | 10    | 10   |
| Concentration of chromium (mg/ml) | 0     | 2    | 4     | 6     | 8     | 10   |
| Volume of DPC solution (ml)       | 0.5   | 0.5  | 0.5   | 0.5   | 0.5   | 0.5  |
| Optical density at 540nm          | 0.00  | 0.02 | 0.11  | 0.34  | 0.62  | 1.07 |
| % of chromium content             | 0.00  | 1.87 | 10.28 | 31.78 | 57.94 | 100  |

(c)

Fig. 1. (a) Different concentrations of Cr (VI) solutions were prepared and optical density of the solutions were found using DPC solution. The % of chromium contents were found in (b) and (c).

Maximum OD value was considered as 100%. Based on this, other OD values were calculated.

5.2. Batch studies:

5.2.1. Effect of adsorbent dosage in Cr (VI) uptake:

The effect of biosorbent dosage on Cr (VI) removal at room temperature was investigated by varying the amount of sorbent from 0.5–8.0 g/L and agitated at 120 rpm for 96 h using initial Cr (VI) concentration of 10 mg/ml and at pH value of 10.

The highest uptake was obtained at 7.5 g/L for alkaline treated biosorbents at 100% and 5 g/L for acid treated peels at 93.38% uptake for modified sweet lime peels. Comparatively, the raw Mousambi peels showed lowest uptake at 80% (5 g/L), respectively. The removal of Cr (VI) ions increased with the biosorbent dosage and the equilibrium was attained at 7.5 g/L of adsorbent dosage. This is due to availability of more biosorbent sites and enhanced surface area. In the current study, Cr (VI) uptake increased markedly with 7.5 g/L adsorbent dosage and decreased with 0.5 g/L of adsorbent dosage, i.e., Cr (VI) ions compete for the available biosorbent sites (Fig. 2). Similar results were absorbed by Liang *et al.*,<sup>8</sup> Moussavi and Barikbi,<sup>9</sup> Demirbas *et al.*<sup>10</sup> and Tunali *et al.*<sup>11</sup>

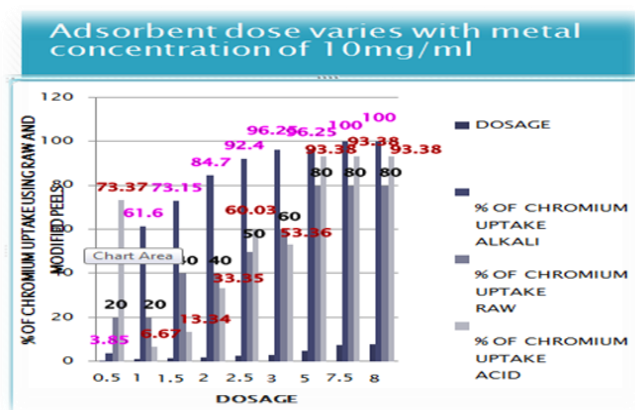


Fig. 2. Graph showing varying effect of adsorbent dosage in Cr (VI) uptake.

5.2.2. Effect of metal concentration:

Effect of initial Cr (VI) ion concentration on its removal was carried out at an adsorbent dose 7.5 g/L, contact time (96 h) and a pH (10) at room temperature by varying the metal ion concentration from 25–100 mg/L. At lower Cr (VI) concentration, the number of moles of metal ions to the available surface area is smaller. However at higher

concentrations, the available sites of adsorption becomes fewer and hence the % of removal of metal ions depends upon the different concentrations of the biosorbent dosage. It also showed that the adsorption was rapid at initial stages up to 25 mg/L and gradually decreased with progress of adsorption (Fig. 3). Similar results were obtained by Namashivayam and kumar.<sup>12</sup> This attributed to the saturation of sorption sites on adsorbents. The initial concentration (25 mg/L) provides a significant driving force to overcome all mass transfer resistance, metal ion between aqueous and solid phases. Hence, a higher concentration of Cr (VI) increases the rate of biosorption.<sup>13</sup>

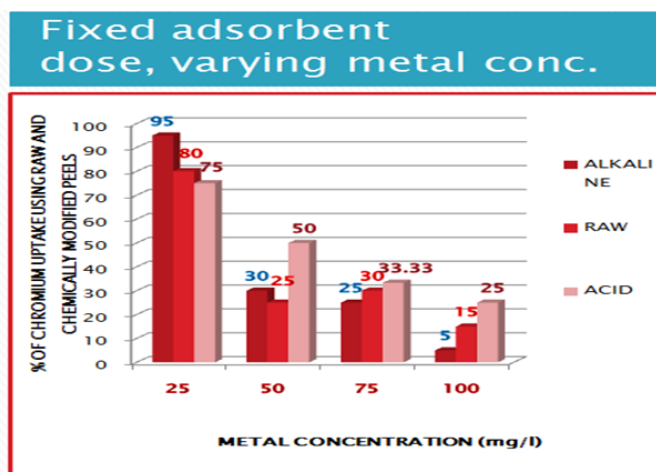


Fig. 3. Graph represents effect of metal concentration.

5.2.3. Effect of contact time:

The time required for biosorption of Cr (VI) on 7.5 g/L raw and chemically modified sweet lime peels were studied. The initial concentration was kept constant at 25 mg/L and pH was set at 10. The experimental data indicates that Cr (VI) ion adsorption increased with increasing contact time. This is due to prolonged contact between the sorbent surface and the Cr ion. The adsorption capacity sharply increased with increase in time and attains 80.04% for alkaline treated peels in 96 h, 71.64% uptake for acid treated peels in 24 h and 75% uptake for raw peels in 24 h and 96 h, respectively (Fig. 4).

The rate of adsorption is different for chemically-modified and raw peels. The rate of adsorption is higher within the first 24 h due to large available surface area of biosorbents. The rate of uptake is also controlled by the rate at which the adsorbate is transported from exterior to the interior sites of biosorbent particles<sup>14</sup> which concludes the rate of adsorption is higher at 96 h. The results also indicate that chemically modified alkaline treated peels showed better sorption capacity than the acid treated and raw *C. limetta* peels.

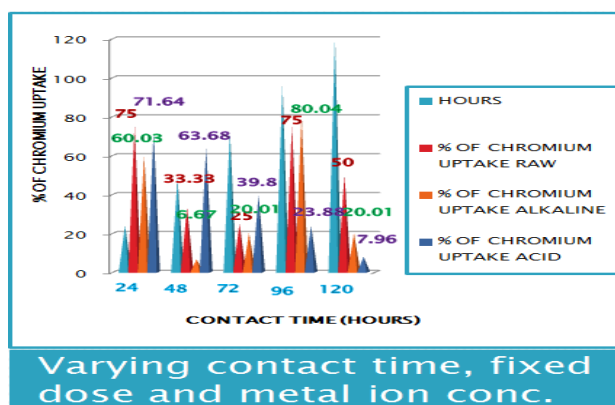


Fig. 4. Graph represents the effect of varying contact time.

5.2.4. Effect of pH in Cr (VI) uptake:

The pH of the solution affects the protonation of the functional group on biomass as well as metal chemistry. Removal of Cr (VI) at varying pH range applying an initial constant Cr (VI) concentration 25 mg/ml, biosorbent concentration of 7.5 g/L and contact time of 96 h. Maximum adsorption of Cr (VI) was observed at a pH 10 for alkali and acid treated biosorbents and significantly decreased by increasing the pH value up to 12. This observation is attributed to the fact that

at low pH value, the adsorption is low due to competition between the  $H^+$  ions and  $Cr^{6+}$  ions. By increasing the initial pH, the dissociation degree of hydroxyl group is increasingly resulting in a higher adsorption ratio by the electrostatic interaction with cations ( $Cr^{6+}$ ). Based on three results, pH of 10 was selected as optimum value for analyzing the influence of other parameters of Cr (VI) ions removal from aqueous solution through chemically modified and raw peels. At pH 10, uptake yield % was found to be 100% and 92.9% for alkaline and acid treated sweet lime peels in 96 h and for raw peels 100% in 24 h at pH 2 (Fig. 5). According to Vijayraghavan and Yun,<sup>15</sup> pH of aqueous solution plays a significant role in the biosorption process. This is partially due to strong competing adsorbent. These results suggest that pH affects the solubility of metal ion and ionization state of functional groups<sup>16</sup> like carboxylate, phosphate and amino groups on cell wall of biosorbents.<sup>17-19</sup>

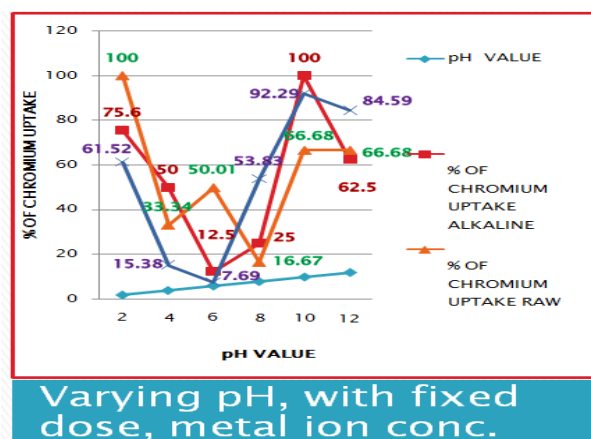


Fig. 5. Effect of the various pH on adsorption.

### 5.2.5. Effect of Temperature in Cr (VI) uptake:

From the biosorbed metal concentration, 25 mg/ml by sweet lime peels from solution of Cr (VI) at different temperatures. Room temperature had significant impacts on bioremoved metal ions reduction of this heavy metal resulting in biosorption capacity up to 30–40°C, where low temperature and higher temperature did not show significant result in both chemically modified and raw peels at 96 h (Fig. 6). These contrasting values may be related to several variables such as sorbent species, quantity and other environmental factors. However, the adsorption species might have enough energy of the system and subsequently be desorbed at even faster rate than adsorption rate or may be due to linkage of cells in both higher and lower temperature extremes which may reduce the availability of surface area of contact.<sup>19</sup>

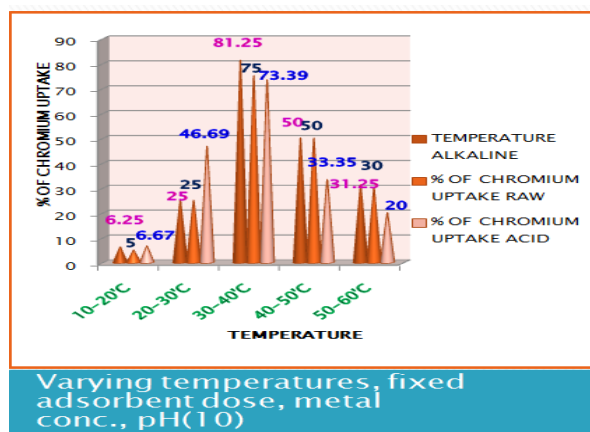


Fig. 6. Effect of the various temperature on Cr (VI) adsorption.

## 5.3. Characterization of biosorbents:

### 5.3.1. Fourier transform infrared spectrum:

FT-IR spectroscopy method was used to show the functional groups present on the surface of the peels. Figure 7(a) (1A, 1B and 1D) shows FT-IR spectra of raw and chemically modified peels before adsorption. Looking at the spectra, it shows band shifting and possible involvement of OH group around broad peak 3418 and 3425  $cm^{-1}$ . The peak at 2922,



1302–1470  $\text{cm}^{-1}$  and 2923  $\text{cm}^{-1}$  is due to CH stretching vibrations. The peak at 1742, 1743 and 1736  $\text{cm}^{-1}$  is due to C=O stretching. Apart from this major change, there is vibration of C–OH alcohols and –OH binds to the peak 2922 and 2923  $\text{cm}^{-1}$  in the raw peels and acid treated peels, whereas OH binding is absent in the alkali treated peels. Similar C=O stretching and –OH binding were reported in orange juice residues.<sup>20</sup>

For biosorption of Cr (VI) ions on to sweet lime residue as shown in Fig. 7(b) (1C, 1D and 1F), there is a major difference in the region 690–850  $\text{cm}^{-1}$  and 610–700  $\text{cm}^{-1}$ . These results indicate that after the biosorption of Cr (VI) is significantly distorted suggesting chemical interaction that occurs between metal ions and the –OH group on the biosorbent surface. The bands at around 610–680  $\text{cm}^{-1}$  where the characteristics of inorganic group in the alkali and acid treated sample, whereas absent in raw peels but inorganic groups were observed after Cr (VI) uptake in raw peels. The peak at 3200–3500  $\text{cm}^{-1}$  (stretching of –OH group) was involved in asymmetric stretching. Slight shifting was observed on the C–H band at the peak 1600–2000  $\text{cm}^{-1}$ , 1320–1440  $\text{cm}^{-1}$  and 730–770  $\text{cm}^{-1}$ . C–H stretching mode represents the aliphatic nature of peels. The adsorption bands at 1620–1680  $\text{cm}^{-1}$  were characteristics of C=C in aromatic rings. Similar C–H stretching and adsorption bands for C=C in aromatic rings were observed by Friedman and Waiss<sup>21</sup> and Sulak *et al.*,<sup>22</sup>

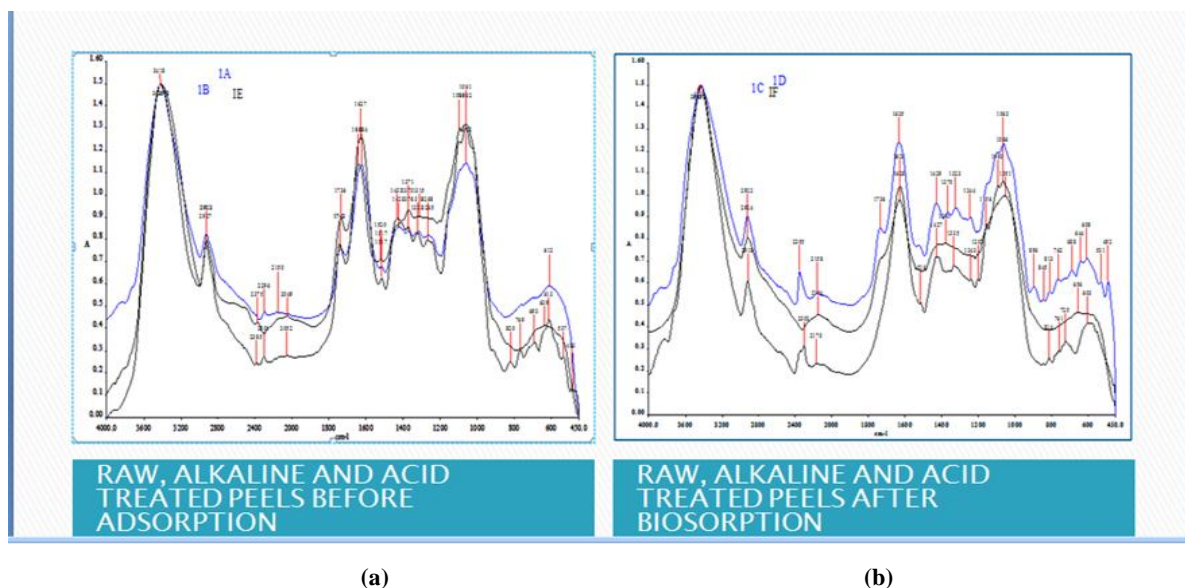


Fig. 7. The FTIR studies

### 5.3.2. Scanning Electron Microscopy:

SEM images of the biosorbents showed that the surface of the biomaterial present some cavities throughout the surface of *C. limetta* fruit shell, indicating that this material present good characteristics to be employed as a natural adsorbent for metallic ion uptake (Cr (VI)). The SEM of *C. limetta* peel powder before Cr (VI) adsorption (raw peels) and after Cr (VI) adsorption (raw and chemically modified peels) is shown in Figs. 8 (a)–8 (d). The surface morphology revealed that both the materials was found to be irregular and porous and thus would facilitate the adsorption of metal ions on different parts of the material. Similar structure and morphology were observed on orange peels.<sup>23</sup> The SEM micrograph showed that cavities with different sizes and different shapes existed on external surface of *C. limetta* peel powder. Similar cavities were previously reported by Abu-El-Sha'r *et al.* After alkali treatment, SEM micrograph has more deposition towards the cavities than the raw control and acid treated peels. The micrograph of *C. limetta* peel powder after Cr (VI) adsorption shows a reduction of number of pore space and surface area available. Hence, it is confirmed that there is metal adsorption on the surface of adsorbent.

### 5.3.3. Energy dispersive X-ray analysis:

EDX analysis of *C. limetta* peels has been represented in Figs. 8 (a)–8 (d). It showed the % weight of the chemical composition on the surface of *C. limetta* fruit peels were as follows: refer Tables from Figs. 8 (a)–8 (d). The EDX peels demonstrate that the existence of Cr (VI) metal on the peel surface. The original peels exhibit no adsorption for Cr (VI) metal uptake whereas alkaline treated peels showed maximum adsorption for Cr (VI) compared to acid treated peels and raw peels. All these results reveal that the waste peels of *C. limetta* had adsorbed the metal ion (Cr (VI)). Similar results were reported in custard apple peels by Krishna and Padma Sree.<sup>24</sup>

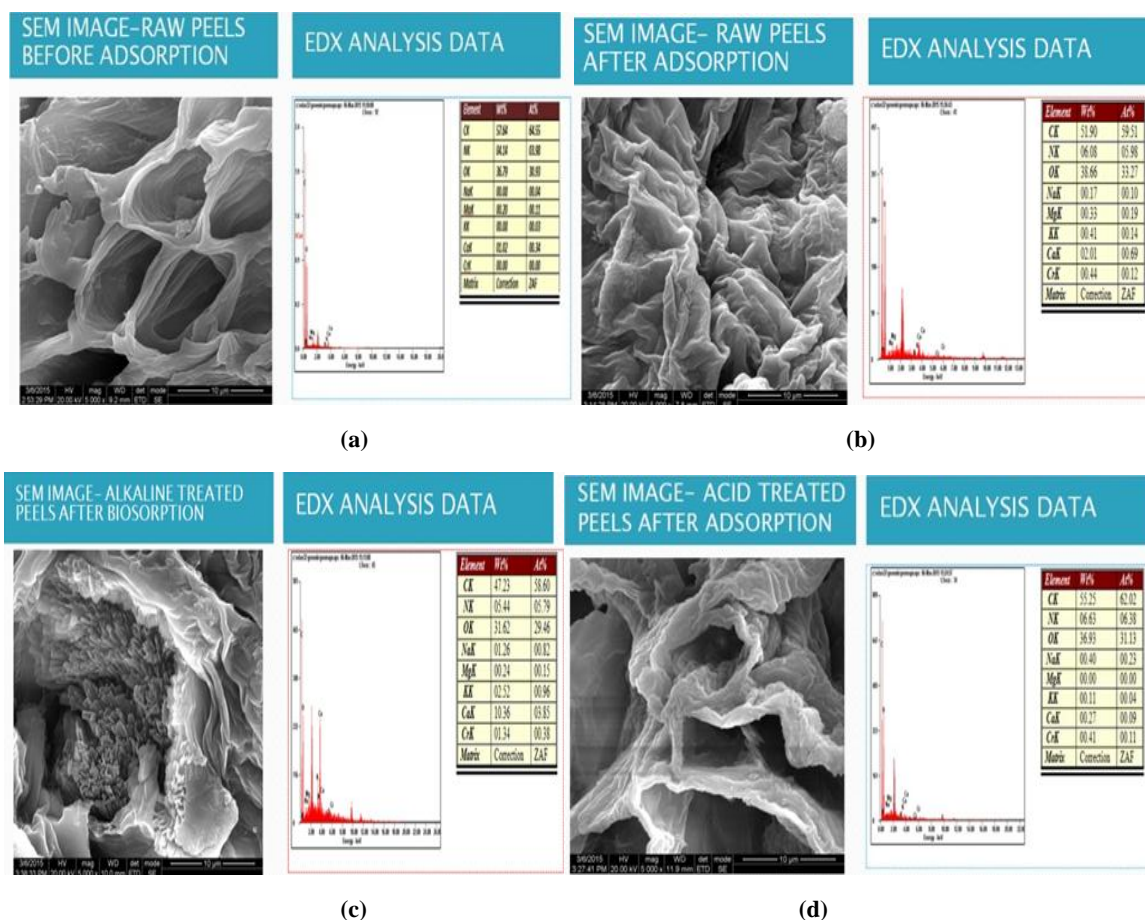


Fig. 8. SEM and EDX analysis.

## 6. TREATMENT OF INDUSTRIAL EFFLUENT

Industrial effluent provided from Nagalkeni tannery station and chrome liquor waste from Central Leather Research Institute was tested for adsorptive recovery of Cr (VI) utilizing alkaline treated using *C. limetta* peels. The optimized batch parameters were introduced to adsorb Cr (VI) in sample.

## 7. CONCLUSION

The comparative efficiency of alkaline, acid and raw peels of Musambi in removal of Cr (VI) from its synthetic solution in batch modes proved alkaline treated peels to be more effective. The optimum adsorbent dose, metal ion concentration, contact time, pH and temperature were found to be 7.5 g/L, 25 mg/mL, 96 h, 10°C and 30–40°C, respectively, with a agitation speed of 120 rpm. Peaks corresponding to the hydroxyl and carboxyl groups (metal ion and —OH), inorganic groups, and bands around the region 610–680 cm<sup>-1</sup> were observed after Cr (VI) adsorption to peels. SEM micrographs of alkaline treated peels have more deposition towards the cavities than raw and acid treated peels. The micrograph of peels after Cr (VI) adsorption shows reduction of number pore space and surface area available. The EDX results demonstrate the existence of Cr (VI) metal on alkaline treated peel surface (1.34%).

## ACKNOWLEDGMENTS

We acknowledge our sincere thanks to IIT Madras, Department of Biotechnology.

## REFERENCES

- [1] Thakur SI (2011), Environmental Biotechnology: Basic concepts and Applications, New Delhi: I. K. International.
- [2] Lindberg E, Hedenstierna G (1983). Chrome plating: symptoms, findings in the upper airways, and effects on lung function. Arch. Environ. Health 38(6):367–374.

- [3] Dayan AD, Paine AJ (2001). Mechanism of chromium toxicity, carcinogenicity and allergenicity: review of literature from 1985 to 2000. *Hum. Exp. Toxicol.* 20:439–451.
- [4] Langard S, Norseth T (1975). A cohort study of bronchial carcinomas in workers producing chromate pigments. *Br. J. Ind. Med.* 32:62–65.
- [5] Malkoc E, Nahoglu Y (2005). Investigations of Ni(II) removal from aqueous solutions using tea factory waste. *J. Hazard. Mater.* 127:120–128.
- [6] Alikarami M, Abbasi Z, Mohammadnezhad S (2013). Kinetics and thermodynamics studies of Copper (II), Mercury (II) and Chromium (III) Adsorption from aqueous solution by peels of banana. *J. Basic. Appl. Sci. Res.* 3(3):8–15.
- [7] Thomas GC (1993). *Qualitative and Instrumental Analysis of Environmentally Significant Elements*. New York: John Wiley & Sons, p. 43.
- [8] Liang S, Guo X, Feng N, Tian Q (2009). Adsorption of Cu<sup>2+</sup> and Cd<sup>2+</sup> from aqueous solution by mercapto-acetic acid modified orange peel. *J. Colloids Surf. Biointerfaces* 73:10–14.
- [9] Moussavi G, Barikbin B (2010). Biosorption of Cr (VI) from industrial waste water on to Pistachio hull waste biomass. *Chem. Eng. J. Hazard. Mater.* 182:552–556.
- [10] Demirbas M, Kobya M, Konukman AES (2008). Error analysis of equilibrium studies for the almond shell activated carbon adsorption of Cr (VI) from aqueous solution. *J. Hazard. Mater.* 154:787–794.
- [11] Tunali S, Kiran I, Akar T (2005). Cr (VI) biosorption characteristics of *Neurospora crassa* fungal biomass. *Mining Eng.* 18:681–669.
- [12] Namasivayam C, Kumar MVS (2008). Removal of Cr (VI) from water and waste water using surfactant modified coconut coir pith as a biosorbent. *Bioresour. Technol.* 99:2218–2225.
- [13] Donmez D, Aksu Z (2002). Removal of Cr (VI) from saline waste waters by *Dunaliella* species. *Process Biochem.* 38:751–762.
- [14] Habib A, Narul I, Anarul I, Alam AMS (2007). Removal of copper from aqueous solution using orange peels, sawdust and bagasse. *Pak. J. Anal. Environ. Chem.* 8(1&2):21–25.
- [15] Vijayraghavan KJ, Yun YS (2008). Bacterial biosorbents and biosorption. *Biotechnol. Adv.* 26:266–291.
- [16] Lu D, Cao Q, Li X, Cao X, Luo F, Shao W (2008). Kinetics and equilibrium of Cu (II) adsorption on to chemically modified orange peels cellulose biosorbents. *Hydrometallurgy* 64:112–127.
- [17] Saikaew W, Kaewsarn P (2009). Cadmium ion removal using biosorbents derived from fruit peel wastes. *Sonklanakarin J. Sci. Technol.* 31(5):547–554.
- [18] Cordo B, Loderio P, Herrero R, de Vicente MES (2004). Biosorption of Cd by *Fucus spiralis*. *Environ. Chem.* 1:180–187.
- [19] Zvinowwanda CM, Okonko JO, Agyei NM, Shabalala PN (2009). Physicochemical characterization of Maize tassel adsorbent: part 1, surface texture, microstructure and thermal stability. *J. Appl. Poly. Sci.* 2:1923–1930.
- [20] Paudyal H, Hu Q, Zhao J, Huo F, Inoue K, Liu H (2014). Adsorptive recovery of Vanadium (V) from Chromium (VI) containing Zr (IV) loaded orange juice residue, *Chem. Eng. J.* 248:79–88.
- [21] Masri MS, Friedmar M (1973). Competitive binding of mercuric chloride in dilute solutions by wool and polyethylene or glass container. *Environ. Sci. Technol.* 7: 951–953.
- [22] Sulak MT, Demirbas E, Kobya M (2006). Removal of Astrazon yellow 7GL from aqueous solutions by adsorption onto wheat bran, *Bioresour. Technol.* 98:2590–2598.
- [23] Lai Y-L, Thirumavalavan M, Lee J-F (2010) Effective adsorption of heavy metal ions (Cu<sup>2+</sup>, Pb<sup>2+</sup>, Zn<sup>2+</sup>) from aqueous solution by immobilization of adsorbents on Ca alginate beads. *Toxicol. Environ. Chem.* 92:697–705.
- [24] Krishna D, Sree RP (2013). Removal of chromium from aqueous solution by custard apple peels powder as adsorbent. *Int. J. Appl. Sci. Eng.* 11(2):171–194.