J. Plantarum., 7(1): 33-42
ISSN PRINT 2710-4079
ISSN ONLINE 2710-4087

REMOVAL OF COPPER HEAVY METAL BY USING BIOSORPTION TECHNIQUE

AYESHA SHAFQAT[1], SUNDUS AKHTAR[1*], IQRA YOUNIS[1], TABASSUM GULL[1], AMMARA MUKHTAR[1], AREEBA AQEEL[1], ATIYA TASNEEM ASIF[1]

School of Biology (Botany Section), Minhaj University Lahore
**Corresponding author's Email: dr.sundas@mul.edu.pk*

Received on: 23-11-24; Reviewed on: 21-04-25; Accepted on: 12-05-2025; Published on: 15-06-2025

Abstract

The suitability of agricultural waste material such as Orange (*Citrus sinesis* L.), Lemon (*Citrus limon* L.), and mousami (*Citrus limetta* Risso.) peels to eliminate heavy metal Cr (VI) was investigated using a batch biosorption technique. The amount of metal ions removed from solution is determined by the contact duration between the metal ion substrate and the ions, as well as the ion concentration and type. For all three substrates, contact times were chosen at 15, 30, and 60 minutes. When compared to other biosorbents, such as mousami peels (76 to 89 pp) shows higher biosorption efficiency as compared to orange and lemon peels i.e.; (40 to 68 ppm) and (44 to 66 ppm) in the aqueous metal solution. In all cases mousami (*C. limetta*) peels exhibited greatest adsorptive capacity for Cr (VI) ions removal than other biosorbent.

Key Words: Heavy metal, Biosorption, lemon, Orange, Mousami, biosorbents

INTRODUCTION

Heavy metals are elements characterized by relatively high atomic weights or numbers and are known for their potential toxicity to living organisms even at low concentrations. However, the classification of an element as a "heavy metal" often depends more on its chemical behavior than just its density (Ali and Khan, 2018). Chromium (Cr) stands out as the seventh most abundant element on Earth and is typically extracted from chromite ore ($FeCr_2O_4$). Its divalent form (Cr^{2+}) is commonly found in concentrations ranging from 10 to 50 mg/kg, varying with the geological parent material, and can accumulate in environmental media such as soil, air, and water. The hexavalent form of chromium (Cr (VI)) is particularly hazardous due to its high solubility, strong oxidative potential, and ability to infiltrate biological systems. Unlike the more stable and less toxic trivalent form (Cr(III)), Cr (VI) mimics essential sulfate ions and is taken up by cells through sulfate transport mechanisms (Mohan and Pittman, 2006).

Chromium, as a toxic heavy metal, can interfere with plant growth by inhibiting cell division and extending the cellular cycle, which often leads to reduced root development. It also negatively impacts photosynthetic efficiency by disrupting carbon dioxide fixation, electron transport, photophosphorylation, and the activity of key photosynthetic enzymes. Elevated levels of chromium in soil and water, stemming from both natural processes and human activities, have made it a serious environmental contaminant. Its accumulation in edible crops grown on contaminated soils poses significant health risks to both humans and animals (Oliveira, 2012). Chromium exposure in plants has been associated with inhibited growth, leaf chlorosis, damage to root cells, reduced pigment levels, impaired water and nutrient uptake, and disruptions in enzymatic functions (Ranieri and Gikas, 2014).

Various strategies have been developed to reduce the availability of heavy metals in soil. Physical, chemical, and biological methods are commonly employed to remove metal ions from aqueous environments. Among these, biosorption stands out as a sustainable and economically viable approach. Biosorption involves the ability of biological materials to bind and remove heavy metals from contaminated water through either metabolic processes or physicochemical interactions (Shamim, 2018).

Fruit and vegetable peel waste (FVP), generated in households and food processing industries, constitutes a large portion of organic waste. Although domestic production is minimal, the volume of waste from food industries is substantial. Due to its rapid decomposition, FVP waste often contributes to problems in landfill management. However, these materials have shown potential as low-cost biosorbents (Patel, 2012). The biosorption method has been particularly explored for the removal of copper, offering a sustainable and effective means of minimizing the environmental and health risks associated with heavy metal pollution.

MATERIALS AND METHODS

Metal Selection

The present study employed a biosorption strategy for the removal of heavy metals from irrigation water, with a particular focus on chromium due to its high toxicity. Potassium dichromate ($K_2Cr_2O_7$) was used as the source of chromium to prepare the stock solution. A 1000 mL chromium stock solution was initially prepared and subsequently diluted with distilled water as needed for the experiments. After each treatment, the concentration of residual chromium ions was measured using an atomic absorption spectrophotometer (AAS).

Biosorption approach

Biosorption is a passive physicochemical process in which contaminants, such as metal ions (biosorbates), attach to the surface of biosorbents derived from biological materials. Due to its low operational cost and high metal-binding capacity, biosorption offers a practical solution for the treatment of industrial wastewater. It is considered an environmentally friendly and economically viable alternative for heavy metal removal. The process holds significant potential, especially when utilizing low-cost or waste materials as biosorbents, making it a widely adopted method. In research applications, evaluating the risks associated with hazardous and non-hazardous waste disposal, along with identifying efficient treatment options, is crucial to ensure the sustainability and effectiveness of biosorption-based techniques.

Selection and Preparation of Biosorbents

Peels of orange (*Citrus sinensis*), lemon (*Citrus limon*), and mousami (*Citrus limetta*) were collected from local markets in Lahore, Punjab, Pakistan. The collected biomass was first washed thoroughly with tap water followed by distilled water to remove dirt and impurities. The cleaned peels were then sun-dried for two days in open air on a rooftop, which reduced their moisture content and mass. This drying process also led to noticeable changes in the color of the peels. After sun drying, the peels were further oven-dried at 60 °C for one night to ensure complete moisture removal. The dried biomass was then crushed using a household grinder to obtain a fine powder, which was stored in airtight containers for further experimental use.

Preparation of Chromium Stock Solution

A stock solution of chromium was prepared using potassium dichromate ($K_2Cr_2O_7$), which has a molecular weight of 294.18 g/mol. A measured quantity of $K_2Cr_2O_7$ (5.66 g) was dissolved in 1000 mL of distilled water to obtain the stock solution. The mixture was stirred continuously for 5 minutes to ensure complete dissolution. The prepared solution was stored in sealed containers and kept in a safe place for future use. Working solutions with concentrations of 75 ppm and 100 ppm were prepared by diluting the stock solution with double-distilled water. The pH of each solution was adjusted to 7.8 using either 0.1 M NaOH or 0.1 M HCl, and confirmed using a digital pH meter.

Batch Biosorption Experiments

For the biosorption trials, 1 gram of each powdered biosorbent was added separately to flasks containing 100 mL of the chromium solution. The flasks were placed on an orbital shaker set at 150 rpm and maintained at 25 °C for varying contact times (15, 30, and 60 minutes). After the completion of each time interval, the contents were filtered through Whatman No. 42 filter paper. The filtrate was analyzed using an Atomic Absorption Spectrophotometer (AAS) to determine the residual chromium concentration. All experiments were conducted in triplicate to ensure reproducibility. A control setup, containing the metal solution without any biosorbent, was included for comparison. The collected data were statistically analyzed using the Least Significant Difference (LSD) method to evaluate the significance of treatment effects.

RESULTS

In the biosorption experiment, various fruit peels—orange, lemon, and mousami were selected as biosorbents to remove hexavalent chromium [Cr (VI)] from aqueous solutions. The removal process was monitored at different contact times (15, 30, and 60 minutes) to assess time-dependent adsorption efficiency. In addition to measuring chromium uptake by each biosorbent, parameters such as biosorption efficiency, adsorption capacity, and the concentration of residual metal in the solution were also evaluated.

Top of Form

Biosorbents and Bottom of Form

Cr (VI) build up

Orange peels

Figure 1 A shows the results of Cr (VI) build up using orange peels at various intervals. Orange peels absorbed 40 to 67 ppm of Cr (VI) when conc. of this metal was 75 ppm and it increased to 49-76 ppm when a higher level of Cr (VI) was used i.e., 100 ppm.

Lemon peels

Whereas when lemon peels were used, they showed an absorption of 48-66 ppm at 75 ppm concentration of Cr (VI) and 64-79 ppm of heavy metal when 100 ppm of Cr (VI) was used (Figure 1 B). These results are for various intervals of time showing a range of absorption.

Mousami peels

Whereas the use of mousami peels showed an absorption of 53-69 ppm at 75 ppm concentration of Cr (VI) and 76-90 ppm of heavy metal when 100 ppm of Cr (VI) was used (Figure 1 C). These results are for various intervals of time showing a range of absorption.

Residual-metal ion concentration

Orange Peels

The concentration of residual Cr (VI) after treatment with orange peels at an initial concentration of 75 ppm ranged from 35 to 7 ppm over 15, 30, and 60 minutes. At 100 ppm, the remaining metal in the solution decreased from 51 to 24 ppm with increasing contact time, as illustrated in Figure 2A.

Lemon Peels

For lemon peels, the remaining Cr (VI) concentration at 75 ppm ranged from 27 to 9 ppm over the three-time intervals. At an initial concentration of 100 ppm, the residual metal concentration decreased from 35 to 21 ppm after 15, 30, and 60 minutes, respectively (Figure 2B).

Mousami Peels

In the case of mousami peels, the remaining Cr (VI) at 75 ppm was found to be between 22 and 6 ppm. When the initial concentration was 100 ppm, the residual metal in the solution ranged from 23 to 10 ppm across the different time intervals (Figure 2C).

Efficiency of Cr (VI) Removal

Orange Peels

At an initial concentration of 75 ppm, the efficiency ranged from 47 to 9 ppm over 15, 30, and 60 minutes. When the Cr (VI) concentration was increased to 100 ppm, the removal efficiency varied from 51 to 24 ppm across the same time intervals, indicating improved performance with prolonged exposure (Figure 3A).

Lemon Peels

As shown in Figure 3B, lemon peels exhibited Cr (VI) removal efficiency ranging from 36 to 12 ppm at 75 ppm initial concentration. At 100 ppm, the efficiency ranged from 35 to 21 ppm at 15, 30, and 60 minutes, respectively, suggesting consistent biosorption behavior with time and concentration.

Mousami Peels

Figure 3C illustrates the Cr (VI) removal efficiency of mousami peels. At 75 ppm, the efficiency ranged from 29 to 8 ppm over the three contact times. At 100 ppm, the removal efficiency varied between 23 and 10 ppm over 15, 30, and 60 minutes, showing moderate biosorption potential.

Biosorption Capacity

Orange Peels

The biosorption capacity of orange peels for Cr (VI) at an initial concentration of 75 ppm ranged from 3500 to 700 ppm over 15, 30, and 60 minutes. At 100 ppm, the capacity increased, varying between 5100 and 2400 ppm during the same time intervals (Figure 4A).

Lemon Peels

Lemon peels demonstrated a biosorption capacity ranging from 2700 to 900 ppm at 75 ppm Cr (VI). When exposed to 100 ppm Cr (VI), their capacity ranged from 3500 to 2100 ppm across the different contact times (Figure 4B).

Mousami Peels

Mousami peels showed a biosorption capacity of 2200 to 600 ppm at 75 ppm Cr (VI). At the higher concentration of 100 ppm, the capacity ranged from 2300 to 1000 ppm over 15, 30, and 60 minutes (Figure 4C).

Comparative Analysis of Cr (VI) Biosorption

At 75 ppm

Figure 5A presents the comparison of biosorption of Cr (VI) using three different biosorbents at an initial concentration of 75 ppm. The results indicate that mousami peels exhibited the highest uptake, absorbing between 53 and 69 ppm of Cr (VI). This was followed by lemon peels with absorption values ranging from 44 to 66 ppm, and orange peels absorbing between 40 and 68 ppm. The overall trend for Cr (VI) biosorption at 75 ppm was mousami peels > lemon peels > orange peels.

At 100 ppm

Comparative biosorption at 100 ppm, illustrated in Figure 5B, showed that mousami peels again achieved the highest absorption, ranging from 76 to 89 ppm. Lemon peels followed with absorption values between 64 and 79 ppm, while orange peels absorbed from 49 to 76 ppm of Cr (VI). Hence, the trend at 100 ppm was mousami peels > lemon peels > orange peels.

DISCUSSION

In the current study, three different biosorbents—orange, lemon, and mousami (also known as sweet lime) peels—were selected in dried powder form for the biosorption of chromium (Cr VI) from aqueous solutions. These biosorbents demonstrated excellent performance in terms of chromium accumulation, biosorption capacity, and removal efficiency.

The use of citrus fruit peels as biosorbents has gained significant attention due to their natural abundance, low cost, and environmental sustainability. These peels are rich in various functional groups such as hydroxyl, carboxyl, and pectin, which facilitate the binding of metal ions. The effectiveness of these biosorbents stems from their ability to form complexes with metal ions via multiple mechanisms, including ion exchange, chelation, and electrostatic interactions.

For example, ion exchange involves the replacement of native cations (e.g., Na^+, K^+) on the biosorbent surface with chromium species. Chelation refers to the formation of stable complexes between Cr (VI) ions and functional groups such as carboxyl and hydroxyl groups. Electrostatic interactions depend on the surface charge of the biosorbents, which varies with pH and influences the attraction of negatively charged Cr (VI) species like $HCrO_4^-$ and $Cr_2O_7^{2-}$. Additionally, some biosorbents can facilitate the reduction of toxic Cr (VI) to the less harmful Cr(III), which binds more readily to the biomass (Kannan and Sundaram, 2001).

Different fruit peels may exhibit varying affinities toward specific heavy metals. For instance, Gupta *et al*. (2010) studied the biosorption of zinc (II) using sweet lime (mosambi) peels. Comparative analyses of orange, lemon, and mousami peels highlight their relative biosorption efficiencies. Prior research has also demonstrated lemon peel's capacity to adsorb copper (II) ions effectively (Rajalakshmi *et al*., 2010), showcasing the versatility of citrus peels as low-cost biosorbents.

In the present study, increasing the chromium concentration from 75 ppm to 100 ppm improved biosorption efficiency across all tested peels. Among these, mousami peels consistently exhibited the highest Cr (VI) uptake at both concentrations, followed by lemon and orange peels, establishing the trend: mousami > lemon > orange.

Further insights into the biosorption process can be gleaned from equilibrium modeling and thermodynamic studies. For example, Bishnoi *et al*. (2006) investigated the removal of Ni(II) using orange peel, which helped identify factors controlling biosorption efficiency under varying conditions (Asgher and Bhatti, 2012).

Using fruit peels as biosorbents aligns with green chemistry principles, offering an environmentally friendly alternative to conventional heavy metal removal methods. Their biodegradable nature reduces environmental impact. However, challenges remain, such as biosorbent regeneration, reusability, and handling of spent biomass.

Future research should focus on optimizing operational parameters, enhancing biosorption capacities through chemical or physical modifications, and developing effective regeneration or disposal strategies to ensure the sustainability and scalability of this approach.

CONCLUSION

Biosorption represents a promising, eco-friendly, and cost-effective technique for removing Cr (VI) from irrigation water and contaminated agricultural soils. Utilizing naturally abundant agricultural waste materials adds value while addressing heavy metal pollution. This method offers high efficiency even at low pollutant concentrations and facilitates the reduction of Cr (VI) to the less toxic Cr(III), making it especially suitable for environmental remediation.

For large-scale applications, issues such as biosorbent regeneration or safe disposal, environmental variability, and the risk of secondary pollution must be tackled. Optimization of process parameters and sustainable management of biosorbents will improve practical feasibility and effectiveness. Overall, biosorption is a key component in integrated strategies to mitigate chromium pollution in agricultural ecosystems, contributing to sustainable water and soil management.

FUNDING STATEMENT

This study was supported by the all authors.

AUTHOR’S CONTRIBUTION

All authors contributed equally.

DATA AVAILABILITY STATEMENT

All the data is primary.

ACKNOWLEDGMENTS

The authors highly acknowledge Minhaj University Lahore for providing the necessary facilities, academic support, and research environment that significantly contributed to the successful completion of this study.

CONFLICT OF INTEREST

The authors declared that the present study was performed in absence of any conflict of interest.

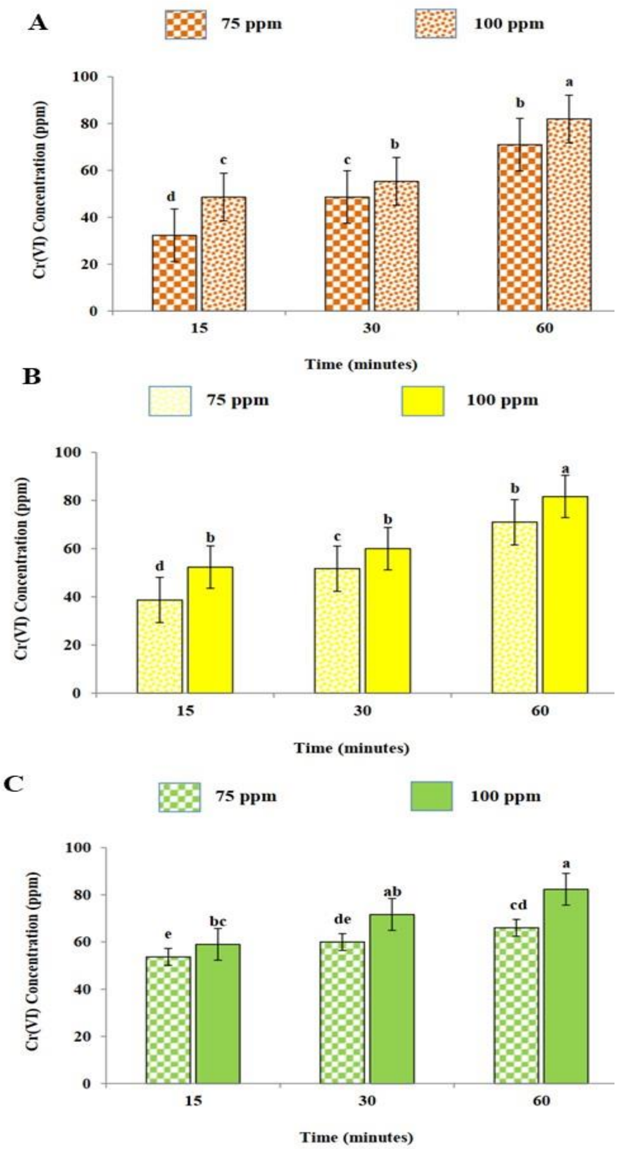

Figure 1 (A to C): Biosorption of Cr (VI) metal by A: orange, B: lemon and C: mousami peels at different time intervals. Columns are representative of the means of three replicates whereas different letters show significant difference in means at $P \leq 0.05$

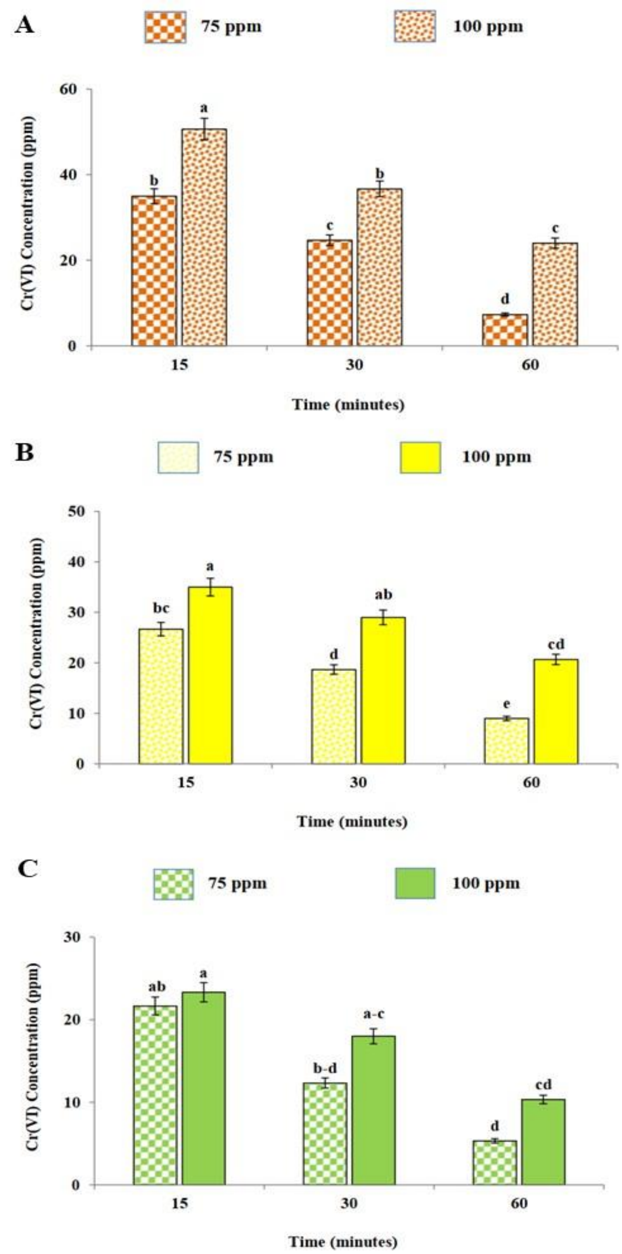

Figure 2: Remaining metal ion concentration by A: orange, B: lemon, C: mousami peels at different time intervals. Columns are representative of the means of three replicates whereas different letters show significant difference in means at $P \leq 0.05$

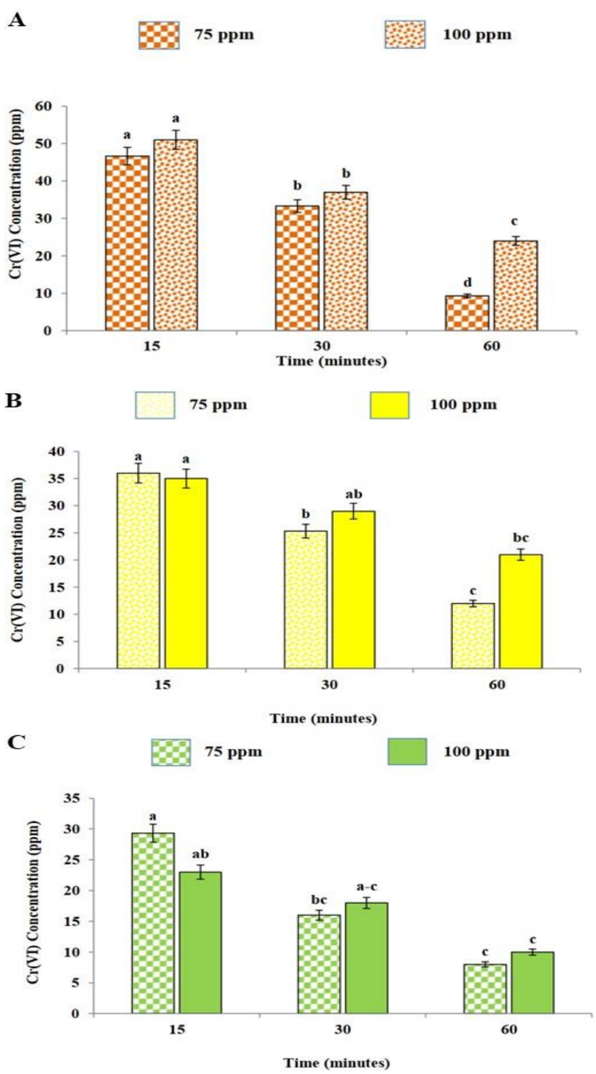

Figure 3 (A to C): Biosorption efficiency by A: orange, B: lemon and C: mousami peels at different time intervals. Columns are representative of the means of three replicates whereas different letters show significant difference in means at $P \leq 0.05$

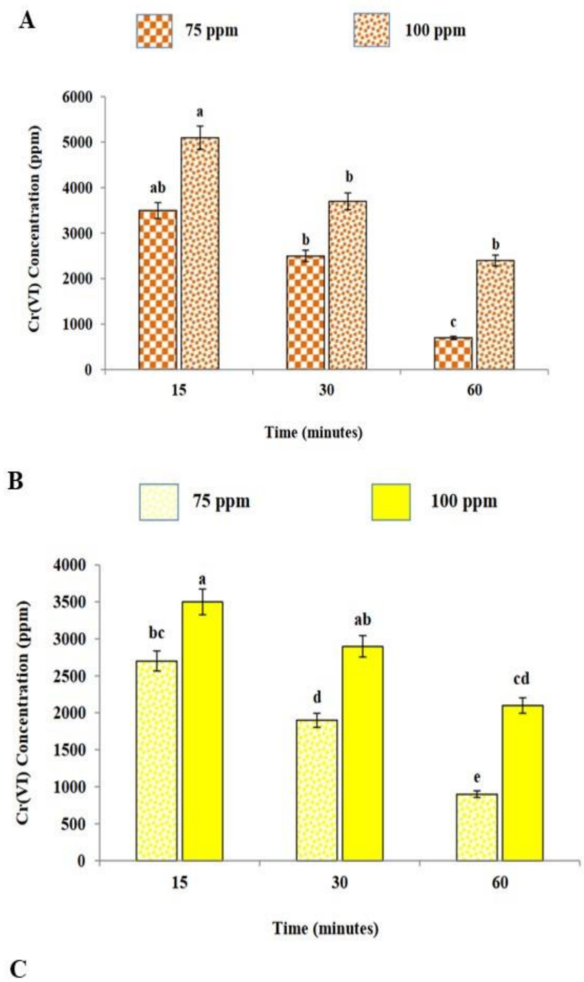

Figure 4 (A to C): Biosorption capacity by A: orange, B: lemon, C: mousami peels at different time intervals. Columns are representative of the means of three replicates whereas different letters are showing significant difference in means at $P \leq 0.05$

ISSN PRINT 2710-4079
ISSN ONLINE 2710-4087

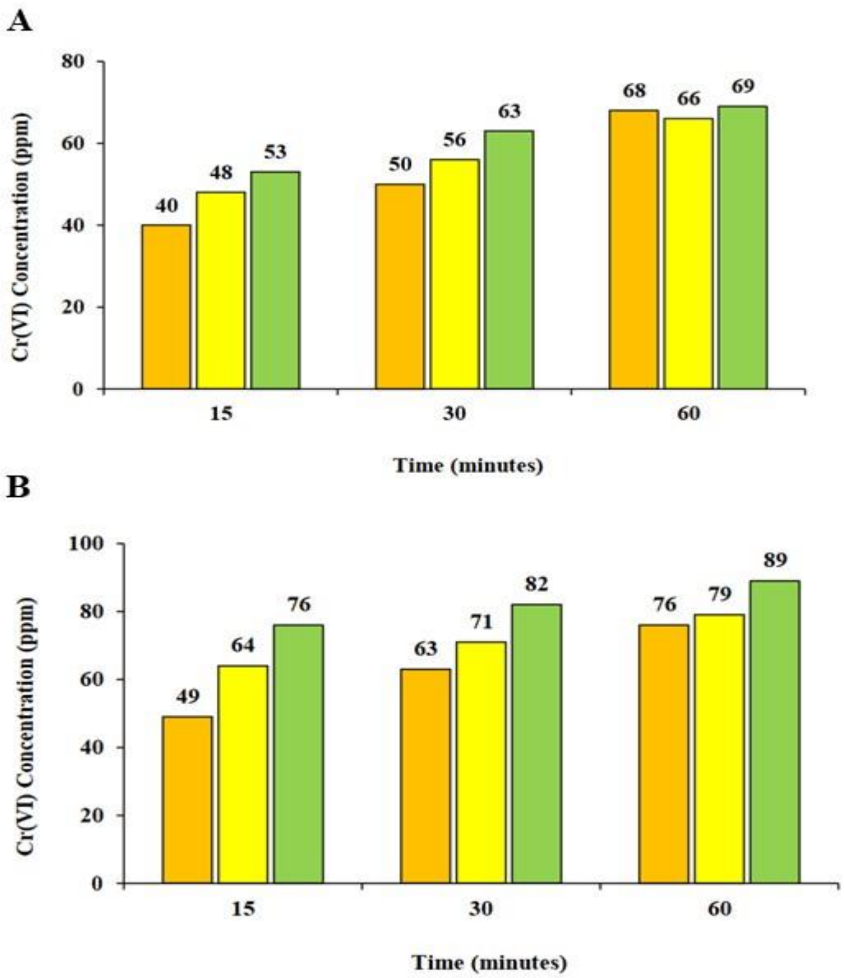

Figure 5 A and B: Comparative analysis of metal absorption through biosorbent at A: 75 ppm B:100 ppm

REFERENCES

Ali, H. and E. Khan. 2018. What are heavy metals? Long-standing controversy over the scientific use of the term 'heavy metals'–proposal of a comprehensive definition. *Toxicological Environmental Chemistry*, 100(1): 6-19.

Asgher, M. and H. N. Bhatti. 2012. Evaluation of thermodynamics and effect of chemical treatments on sorption potential of Citrus waste biomass for removal of anionic dyes from aqueous solutions. *Ecological Engineering* 38(1): 79-85.

Bishnoi, S. R., B. K., Kumar, V. Kumar, A. K. Rana. 2006. Removal of Ni (II) from aqueous solution by adsorption onto orange peel and its equilibrium modeling. *Advances in Environmental Research*, 10(1): 13-23.

Gupta, V. K., A. Rastogi, A. Nayak. 2010. Biosorption of zinc (II) from aqueous solution by sweet lime (Citrus limetta) peel: Equilibrium, kinetics, and thermodynamics studies. *Chemical Engineering Journal*, 162(1): 122-131.

Kannan, N., M. M. Sundaram. 2001. Biosorption of heavy metals from aqueous solutions by orange peel: Equilibrium and kinetic studies. *Process Biochemistry*, 37(1): 87-96.

Mohan, D. and C. U. Pittman Jr. 2006. Activated carbons and low cost adsorbents for remediation of tri-and hexavalent chromium from water. *Journal of Hazardous Materials,* 137(2): 762-811.

Oliveira, H. 2012. Chromium as an environmental pollutant: insights on induced plant toxicity. *Journal of Botany*, https://doi.org/10.1155/2012/375843

Patel, S. 2012. Potential of fruit and vegetable wastes as novel biosorbents: summarizing the recent studies. *Reviews in Environmental Science and Bio/Technology* 11(4): 365-380.

Rajalakshmi, R., R. Rajasekaran, S. S. Rajagopal. 2010. Lemon peel as a low-cost adsorbent for the removal of copper (II) from aqueous solution. *Journal of Environmental Management*, 91(8): 1807-1810.

Ranieri, E. and P. Gikas. 2014. Effects of plants for reduction and removal of hexavalent chromium from a contaminated soil. *Water, Air, Amp; Soil Pollution* 225(6): 1-9.

Shamim, S. 2018. Biosorption of heavy metals. *Biosorption*, 2: 21-49.