



## REMOVAL OF CHROMIUM ION BY CHEMICAL MODIFIED KINNOW PEEL AND IT'S ISOTHERM STUDY

Bhawna Walia<sup>1</sup>, Amita Gupta<sup>2</sup>, Anupama Sharma<sup>3</sup>, Sumit Kumar  
Gupta<sup>4</sup>, Narendra Singh<sup>5</sup>, Manmohan Singh Chauhan<sup>6</sup>, Narendra Pal  
Lamba<sup>7</sup>

---

**Article History:** Received: 05.02.2023

Revised: 20.03.2023

Accepted: 05.05.2023

---

### Abstract

Heavy metals have become a significant source of water contamination due to their poisonous nature and difficulties in biodegrading. Banana peel was employed as a bioadsorbent in this study to remove heavy metals from contaminated water. The fundamental issue with banana peel bioadsorbent is that biomass-derived activated carbon has a far lower adsorption capacity than commercial activated carbon. Furthermore, a large amount of wasted banana peels complicates disposal. Thus, it is anticipated that the current effort will address banana peel disposal issues by converting banana peels into bioadsorbent. The goals of this project are to create a bioadsorbent from banana peels and test its efficacy in adsorbing heavy metals. Furthermore, we optimised the pH, solution temperature, adsorbent dose, contact time, and solid-liquid ratio to assess the bio-capacity adsorbent's to remove Ni. Due to their ease of processing, wide availability, and environmental friendliness, it is strongly suggested that affordable raw materials be used extensively as bioadsorbent in wastewater operations.

---

<sup>1,5,6,7</sup>Amity University Jaipur, Rajasthan, India – 303002

<sup>2</sup>Agarwal P.G. College, Jaipur, India – 302004

<sup>3,4</sup>St., Wilfred's College, Jaipur, India- 302020

**DOI: 10.31838/ecb/2023.12.s3.573**

## 1. Introduction:

Large amounts of heavy metals are created during industrial processes, which damage the environment. Metal ions are not biodegradable, and many of them are readily available to living things because they are soluble in aqueous fluids. Heavy metals are responsible for a variety of diseases in plants and animals, making their removal from aqueous media both crucial and difficult [1,2]. Hexavalent Cr(VI) and trivalent Cr(III) are the two oxidation states of chromium that exist in aqueous media, and the toxicity of chromium is dependent on the oxidation state. Depending on the pH of a solution, Cr(VI) can exist in chromate ( $\text{Cr}_2\text{O}_4^{2-}$ ), hydrochromate ( $\text{HCrO}_4^-$ ), or dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ ), among other forms [3]. Chromium exclusively occurs in Cr(III) in human blood, where it is necessary for the upkeep of blood metabolism. For humans, a daily dietary intake (DDI) of 50–200  $\mu\text{g}$  of chromium is advised [4]. Chromium is used in many different production processes and sectors, including tanneries, paint and pigment factories, electroplating, metal processing, wood preservatives, textile and dye factories, steel fabrication, and canning, and it is released in enormous quantities into the environment [5-7]. Through breathing, eating, drinking, or skin contact with chromium and its components, chromium enters the body. Skin rashes, nasal bleeding, respiratory tract infections, immune system suppression, liver disorders, and lung cancer are just a few of Cr(VI)'s harmful side effects [8,9].

Heavy metals can be removed from aqueous solutions using a variety of techniques, such as chemical precipitation, ion exchange, ultra-filtration, reverse osmosis, and adsorption. Due to the creation of secondary wastes, significant slug formation, and high operational expenses, these technologies do have several drawbacks [10–13]. When employed as heavy metal adsorbents,

agricultural wastes like fruit peels, rice husk, sawdust, baggass, sugar beetroot pulp, soy bean hulls, clay and related minerals have produced better results than other physical and chemical methods [16–19]. Several researches employ cellulosic and lingo-cellulosic materials as effective adsorbents because of their greater capacity for adsorbing metal ions [20,21]. Cellulose, lignin, pectin, and other substances with possible functional groups including hydroxyl, carbonyl, amino, carboxylic, and alkoxy are found in agricultural goods and by-products and have a high affinity for metal ions [22]. For instance, the largest amount of leftover kinnow peels from the fruit processing business contributes to economic and environmental problems solution due to underuse. This biomass is typically thrown away as garbage. Kinnow is frequently eaten as fresh fruit or preserved in juices, jams, and frozen pulp. One of the biggest producers of kinnow is Peru, and the major byproduct, kinnow peel, contains 12–15% pectin on a dry basis. Pectin's ability to fix metal ions via the chemical adsorption process is a result of the pectin's hydroxyl (OH), carbonyl (CO), and carboxyl (COOH) content. This cognition takes into account the accessibility and affordability of this food waste. The purpose of the study was to evaluate whether kinnow peel could be used as an adsorbent material to remove Cr(VI) from polluted aqueous mediums.

## 2. Materials and Methods:

The substance utilised as an adsorbent for the elimination of chromium (VI) is kinnow peel. A desirable and affordable method for removing metal ions from waste water is kinnow peel. The primary substances in kinnow peel include cellulose, pectin, hemicelluloses, and lignin, all of which have functional groups that could serve as metal-binding sites. The nearby market is where the natural adsorbent is purchased. They were then

dried for 24 hours at 70 °C before being washed in alcohol to remove polymer that was not water soluble. The dry samples were ground and sieved through 0.355 mm mesh screens. Sigma-Aldrich was used to provide potassium dichromate, acrylonitrile, ferric sulphate,  $K_2Cr_2O_7$ , sodium hydroxide, sulfuric acid (0.2 N), phosphoric acid (85% by weight), diphenylcarbazide, and chitosan (85% analytical grade).

**Chromium analysis:** The various chromium species present in water were quantified using a colorimetric technique [23]. At 540 nm (UV-2450; Shimadzu, Japan), the pink-colored complex formed by 1,5-diphenyl carbazide and chromium(VI) in acidic solutions was spectrophotometrically examined. Cr(III) was converted to Cr(VI) at high temperatures (130–140 C) prior to the 1,5-diphenyl carbazide reaction in order to quantify the total chromium concentration.

**Acid hydrolysis of Kinnow peel:** Raw kinnow peels (100 g) were placed in a 250 mL flask with 100 mL of 10% HCl solution, and the mixture was heated at reflux for 5 hours. With distilled water, the contents were rinsed until they were neutralised. The glycoside bond in hemicelluloses and lignin depolymerizes during acid hydrolysis by  $\alpha$  and  $\beta$ -aryl ether cleavage to produce soluble molecules.

**Alkaline hydrolysis of Kinnow peel:** Kinnow peels (100 g) were treated with 100 mL of a 10% NaOH solution in a refluxing environment for 5 hours, and then rinsed with distilled water until neutral. Long cellulose chains are broken down into smaller monomers during alkaline hydrolysis.

**Batch experiments for Cr(VI) removal:** Adsorption progress was monitored using a batch technique. To ascertain the impact of various pH, contact time, temperature, and sorbate content, batch sorption investigations were carried out. We employed various concentrations of

biosorbent in a 250 mL stoppered conical flask along with 50 mL of test fluid. By adding HCl and NaOH solution as needed, the pH of the solution was changed. At 125 rpm, the flask's contents were shaken. Following that, the biosorbent was separated from the remaining components of the flask using centrifugation at 15,000 rpm. The amount of residual chromium in the solution was examined.

The remaining chromium concentration in the solution was examined. According to its capability, biosorbent first converts hexavalent chromium to trivalent chromium, which it then adsorbs [24]. The solution should contain trivalent and hexavalent chromium once the biosorbent has been removed. Chromium adsorbed by biosorbent (mg/g) equals the sum of the amount of chromium in the solution prior to adsorption (mg) and the amount of chromium in the solution following adsorption (mg).

### Determination of Metals Uptake Capacity and % Removal

Chromium ion uptake was calculated using the concentration difference method. The adsorption capacity "q" is the amount of metal ion (mg) adsorbed per gramme of KP (dry weight).  $C_i$  (mg/L) represents the initial concentration of metal ions in solution,  $C_e$  represents the equilibrium concentration of metal ions in solution, V(L) represents the volume of the used metal ions solution, and W(g) represents the weight of the adsorbent. The %metal absorption by the sorbent and adsorbent capacity at equilibrium  $q_e$  (mg = g) were calculated using the formulae below.

### 3. Results And Discussion:

**Effect of Biosorbent Particle Size:** The particle sizes of the bio-sorbent had a significant impact on the sorption capacity due to changes in the total surface area available for metal ion sorption. The effect on the sorption capacity, q, of changing the sorbent particle size revealed that smaller

particles removed more Cr ions. The sieve analyzer produced different sizes of bio-adsorbent. Finer bio-adsorbent particles reached equilibrium sooner than bigger ones. This was most likely owing to an increase in total surface area, which supplied more metal ion sorption sites.

Figure 1: Effect of size of adsorbent on removal of Cr ion from aqueous solution.

**Effect of pH:** The pH of the solution influences ion adsorption through influencing the ion speciation and surface charge characteristics of the adsorbents. The maximum removal yield was obtained at acidic pH (pH=4), with values of 64, 82, and 93%. At low solution pH, the high quantity of H<sup>+</sup> and H<sub>3</sub>O<sup>+</sup> protonated from the hydroxyl and carbonyl could outcompete aqueous heavymetal ions for accessible biosorbent binding sites, resulting in little or no adsorption. Higher pH causes deprotonation of functional

groups that serve as binding sites, resulting in improved sorption.

The maximum Cr (VI) removal at 3.4 was most likely due to electrostatic attraction of sorbent surface and hydrogen chromate ions, and that the pH value of The pH of the solution influences ion adsorption through influencing the ion speciation and surface charge characteristics of the adsorbents. The maximum removal yield was obtained at acidic pH (pH=3), with values of 66.81, 83.05, and 61.24%. At low solution pH, the high quantity of H<sup>+</sup> and H<sub>3</sub>O<sup>+</sup> protonated from the hydroxyl and carbonyl could outcompete aqueous heavymetal ions for accessible biosorbent binding sites, resulting in little or no adsorption. Higher pH causes deprotonation of functional groups that serve as binding sites, resulting in improved sorption.

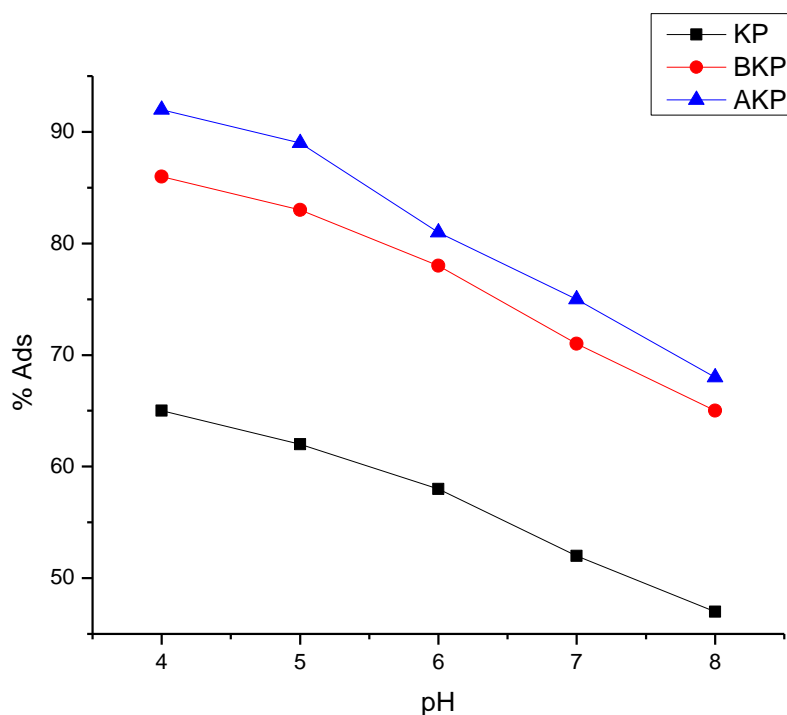


Figure 2: Effect of pH on removal of Cr ion from aqueous solution.

**Effect of agitation speed:** Figure 3 depicts the effect of agitation speed on Cr ion elimination. The agitation speed was kept constant between 50 and 200 rpm.

Other factors such as pH (pH 4), contact length (20 minutes), and temperature (25 degrees Celsius) were remained constant for KP, AKP, and BKP. More Cr ions

were adsorbed (mg/g) as the agitation speed increased. The best results for the removal of Cr ions were discovered with

an agitation speed of 200 rpm. For the remaining experiments, the agitation speed was set at 200 rpm.

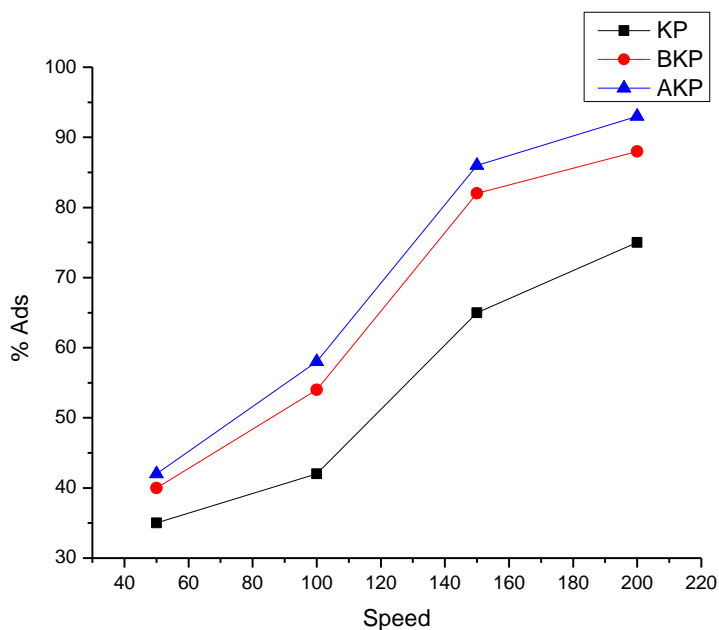


Figure 3: Effect of agitation speed on removal of Cr ion from aqueous solution.

**Effect of adsorbent dose:** Figure 4 depicts the mass of modified and unmodified BP and its effect on the ejection of Cr ion from aqueous solution. Adsorbent dosages for 100 mL of Cr ion solution ranged from 0.1 to 1 g. Temperature (25 degrees Celsius), contact length (20 minutes), and pH (pH 4) were all remained constant. The results show that when adsorbent mass increases, so does Cr ion removal %, while adsorption capacity decreases (Fig. 4). This is because

raising the dosage of modified and unmodified KP makes more active sites available for interaction with metal ions. As a result, the proportion of metal ions eliminated from the aqueous solution increases. On the other hand, aggregation of modified and unmodified KP inside greater doses of adsorbent can lead to unsaturation of active sites, which can lead to a reduction in adsorption capacity. This aggregation reduces the adsorbent's overall surface area.

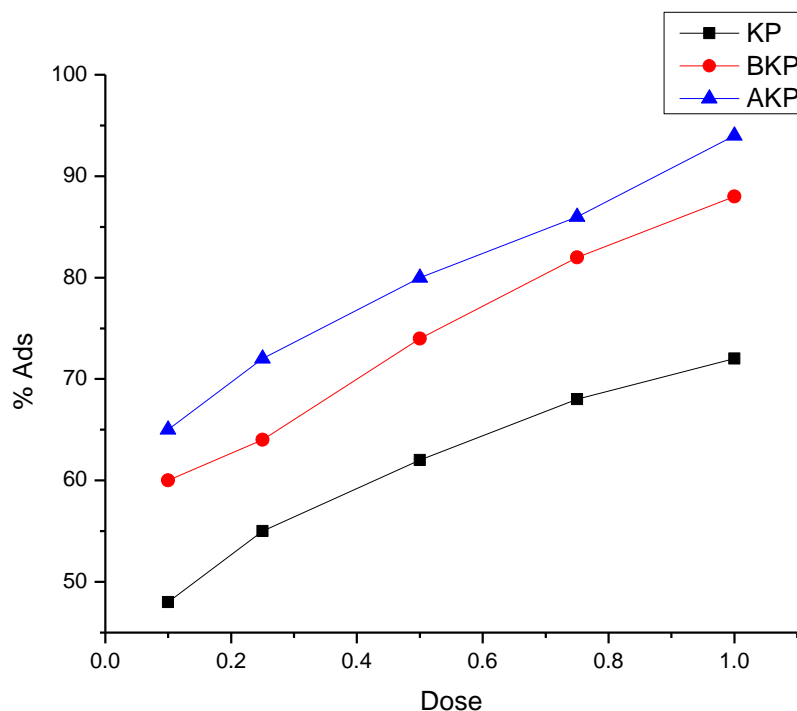


Figure 4: Effect of adsorbent dose on removal of Cr ion from aqueous solution.

**Adsorption Isotherms:** The experimental equilibrium data were modeled using Freundlich model. Freundlich's model depicts the adsorption process on a heterogeneous surface or a surface with several sites and is thus not limited to the creation of a monolayer. This model's mathematical statement is more easily expressed in linear form as:

As illustrated in Fig. 5, linear plots were created by graphing  $\ln q$  vs  $\ln C_e$  with slope  $1/n$ . Fig. 5 was used to calculate the  $n$  and  $K$  ( $L \text{ mg}^{-1}$ ) (adsorption capacity). The " $n$ " values indicate that the adsorbent is efficient; the surface is heterogeneous and has a high affinity for metal ions.

Figure 5: Freundlich's model for removal of Cr ion from aqueous solution.

#### 4. Conclusion:

We created a bio-adsorbent based on recyclable kinnow peel waste to remove chromium ion from aqueous solution. We have a variety of reaction parameters such as pH optimisation, adsorbent dosage, agitation speed, and particle size. Kinnow

peel has been discovered to be a high-capacity, commercially viable, and low-cost cadmium adsorbent.

**Acknowledgement:** We are highly thankful to Amity University Rajasthan for providing technical assistance and also thankful to Amity University Jaipur for providing the financial support.

#### 5. References

1. S. Jiwan, A.S. Kalamdhad, Effects of heavy metals on soil, plants, human health and aquatic life, a review, *Int. J. Res. Chem. Environ.* 1 (2) (2011) 15–21.
2. M. Sprynskyya, B. Buszewski, A.P. Terzyk, J. Namiesnik, Study of the selection mechanism of heavy metal ( $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cd}^{2+}$ ) adsorption on clinoptilolite, *J. Coll. Interf. Sci.* 304 (2006) 21–28.
3. Z.A. AL-Othman, R. Ali, Mu. Naushad, Hexavalent chromium removal from aqueous medium by activated carbon prepared from peanut shell: adsorption kinetics,

- equilibrium and thermodynamic studies, *Chem. Eng. J.* 184 (2012) 224–238.
4. M. Shadreck, T. Mugadza, Chromium, an essential nutrient and pollutant: a review, *Afr. J. Pure Appl. Chem.* 7 (9) (2013) 310–317.
  5. F. Kanwal, R. Rehman, J. Anwar, M. Saeed, Batchwise removal of chromium (VI) by adsorption on novel synthesized polyaniline composites with various brans and isothermal modeling of equilibrium data, *J. Chem. Soc. Pakistan* 34 (5) (2012) 1134–1139.
  6. J.O. Nriagu, E. Nieboer, Chromium in Natural and Human Environment, Springer, New York, NY, USA, 1988.
  7. A.A. Belay, Impacts of chromium from tannery effluent and evaluation of alternative treatment options, *J. Environ. Protect.* 1 (2010) 53–58.
  8. L. Assem, H. Zhu, Chromium General Information, Health Protection Agency, Institute of Environment and Health Cranfield University, 2007, pp. 01–05.
  9. L.S. Zhang, The Advanced Water Treatment and Reuse Technology, Chemical Industry Press, Beijing, 2009.
  10. M.A. Barkat, New trends in removing heavy metals from industrial wastewater, *Arab. J. Chem.* 4 (4) (2011) 361–377.
  11. Y. Bai, B. Bartkiewicz, Removal of cadmium from wastewater using ion exchange resin Amberjet 1200H columns, *Polish J. Environ. Stud.* 18 (6) (2009) 1191–1195.
  12. H.A. Hegazi, Removal of heavy metals from wastewater using agricultural and industrial wastes as adsorbents, *HBRC J.* 9 (3) (2013) 276–282.
  13. [13] D. Lakherwal, Adsorption of heavy metals, a review, *Int. J. Environ. Res. Develop.* 4 (1) (2014) 41–48.
  14. A. Masoumi, M. Ghaemy, Removal of metal ions from water using nanohydrogel tragacanth gum-g-polyamidoxime: isotherm and kinetic study, *Carbohydr. Polym.* 108 (2014) 206–215.
  15. B. Yasmin, T. Zeki, Removal of heavy metals from aqueous solution by sawdust adsorption, *J. Environ. Sci.* 19 (2007) 160–166.
  16. S.C. Ibrahim, M.A.K.M. Hanfiah, M.Z.A. Yahya, Removal of cadmium from aqueous solutions by adsorption onto sugarcane baggas, *J. Agric. Environ. Sci.* 1 (3) (2006) 179–184.
  17. H.S. Londogan, N.E. Arsian, T. Tuman, Copper removal from aqueous solution by sugar beet pulp treated with NaOH and citric acid, *J. Hazard. Mater.* 149 (2007) 433–439.
  18. M.A. Hossain, H.H. Ngo, W.S. Guo, T.V. Nguyen, Removal of copper from water by adsorption onto banana peel as bioadsorbent, *Int. J. GEOMATE* 1 (2) (2012) 227–234.
  19. C. Liu, H.H. Ngo, W. Guo, Optimal conditions for preparation of banana peels, sugarcane bagasse and watermelon rind in removing copper from water, *Bioresource Technol.* 119 (2012) 349–354.
  20. S. Kamel, H. Abou-Yousef, M. Yousef, M. El-Sakhawy, Potential use of bagasse and modified bagasse for removing of iron and phenol from water, *Carbohydr. Polym.* 88 (2012) 250–256.
  21. G. Limousin, J.P. Gaudet, L. Charlet, S. Szenknect, V. Barthes, M. Krimissa, *Appl. Geochem.* 22, 249 (2007).
  22. K. Parvathia, R. Nagendrana, *Sep. Sci. Technol.* 42, 625 (2007).