

Utilization of Ice Apple Fruit Shell Waste Nanocomposites for Removal of Chromium Ion from Aqueous Media

Megha Gang and Shweta Vyas*

(Department of Pure and Applied Chemistry, University of Kota, Kota, Rajasthan, India

*Corresponding Author- [email- shwetavyas@uok.ac.in](mailto:email-shwetavyas@uok.ac.in))

Abstract:

In current work, phosphoric acid (H_3PO_4) activated Ice-apple fruit shell (IFS) is carbonized and then loaded with Nano Iron Oxide (NIO) synthesized using orange peel extracts to prepare NIO@IFSACnanocomposite. Batch experiments were run to study the optimal conditions for maximum removal efficiency for Chromium ion (Cr VI) from aqueous as a capacity of solution pH, solution temperature, stirring time, and Chromium (Cr VI) concentrations. The final concentrations of the Cr VI ions were determined by Atomic Absorption Spectrophotometer (AAS). The optimum conditions were obtained with the achievement of maximum 98% removal of Chromium (Cr VI) ions. These findings demonstrated that NIO@IFSAC can be used as an alluring adsorbent for the effective removal of Chromium (Cr VI) from wastewater in a cost-effective manner. Using such waste materials to prepare nano sorbents would also be a beneficial step toward solid waste management and sustainable development.

Keywords — Activated Carbon, Nanocomposite, Iron Oxide nanoparticles, Ice-apple Fruit shell, Chromium Removal

I. INTRODUCTION

Chromium can exist in several chemical forms displaying variable oxidation numbers from 0 to VI. Only two of them, trivalent (III) and hexavalent (VI), are stable enough to exist in the environment [1]. Cr(IV) and Cr(V) form only as unstable intermediates during reactions of trivalent and hexavalent oxidation states with oxidizing and reducing agents, respectively [2]. Hexavalent Chromium (Cr VI) is known to be carcinogenic and mutagenic and it induces dermatitis [3]. Cr(VI) and Cr(III) enter the environment as a result of effluent discharged from industries like leather, mining, electroplating, dyeing, printing industries, etc. [4, 5].

Chromium can also enter drinking water supply systems via corrosion inhibitors used in water pipes, and containers or via contamination of underground water leaching from sanitary landfill [6]. The maximum permissible limit for hexavalent chromium in drinking water is only 0.05 part per million (PPM) [7] above which it can cause noxious effect in flora and fauna. Hexavalent Chromium (Cr VI) is reported extremely toxic and carcinogenic to trigger cancer of the lungs and digestive system and many abnormalities in routine body functions [8], so it should be checked in wastewater effluents regularly and the excess amount must be removed from contaminated water before being discharged into freshwater resources.

Activated carbon (AC) is microcrystalline black solid, tasteless, non-graphitic carbonaceous material with a porous structure [09]. Adsorption by Activated Carbon (AC) has been reported as a low-cost and simple method for removing various pollutants from water [10, 11]. The two main procedures used to prepare AC from any carbon-rich raw material are physical activation and chemical activation. According to various research reports, chemical activation is preferable over physical activation due to higher yield, larger surface area, and better growth of porous structure [12-15]. Physical activation entails carbonizing a carbonaceous substance and then activating the char which is activated in the presence of activating gases like N₂, CO₂, or steam, while during the chemical activation process, activating substances like acids viz. HCl, H₃PO₄, HNO₃ or bases NaOH, KOH, etc. are impregnated into the raw materials [16-19]. Carbonaceous raw materials, such as coal, lignite, wood, and peat, are typically used in the commercial manufacturing of ACs because of their high carbon content and low inorganic content [20]. Activated carbon from agricultural by-products, on the other hand, has the benefit of delivering an efficient, inexpensive replacement for the non-renewable coal-based granular activated carbons (GACs), so long as they have comparable or superior adsorption efficiency [20-23]. The enormous proportion of very small holes in activated carbon gives it a significant specific surface area [24]

The present study aims to use activated carbon nanocomposites prepared from local waste obtained from Mumbai-Ice-apple fruit shell wastes. Pyrolysis of the ice apple fruit shell wastewas performed with some modifications in the reported method[25], followed by chemical activation using phosphoric acid (H₃PO₄, 85%) as performed by some researchers [26] and loading magnetite nanoparticles on IFSAC by conventional immersion method to obtain an eco-friendly and low-cost Nanocomposite NIO@IFSAC. Batch studies were carried out to determine the maximum adsorption capacity of the prepared nanosorbent for the

removal of Cr (VI) ions from aqueous and to comprehend the effect of pH, temperature, initial metal concentration, adsorbent dosage, and so on. The findings suggested that ice-apple fruit shell waste-based nanocomposites could be used to effectively remove Chromium Ions (Cr VI) from contaminated easy way to comply with the conference paper formatting requirements is to use this document as a template and simply type your text into it.

II. MATERIALS & METHODS

A. Materials

Analytical grade (Sigma Aldrich, India) stock solutions of 1000 mg L⁻¹ concentration of Chromium (VI), The pH of the solution was adjusted by adding 0.1M HCl or 0.1M NaOH (Merk, India) and measured by Systronic digital pH meter, the concentration of Cr(VI) in the aqueous solution was measured using AAS (ice3300 model Thermofischer scientific, 324.75 nm for Cr VI), Double distilled water.

B. Batch Experiments

The batch experiments were carried out to investigate the adsorption capability of NIO@IFSAC (0.250 g) in 50 ml synthetic wastewater of Cr VI ion concentrations at various temperatures, contact times, and pH levels with continuous stirring to ensure homogeneous mixing as shown in Table 1.

TABLE I
BATCH EXPERIMENTAL PARAMETERS FOR BATCH REACTION CONDITIONS

S.No.	Parameters	Units	Range
1.	Cr VI Concentration	ppm	05-30
2.	pH	-	2-08
3.	Contact Time	Minutes	20-180
4.	Temperature	°C	20°C-40°C

The flask containing the sample was withdrawn at the desired time intervals and analyzed by Atomic Absorption Spectrophotometer (AAS, ice 3300-

ThermofischerScientific) for equilibrium Chromium (Cr VI) ion concentrations.

III. RESULTS AND DISCUSSION

A. Effect of Temperature

The effect of temperature on the removal of Cr VI ion by NIO@IFSAC nanocomposite was investigated over a temperature range of 20°C to 40°C. The adsorption efficiency of the adsorbent increased as the temperature increased, demonstrating that the reaction follows the endothermic pathway.

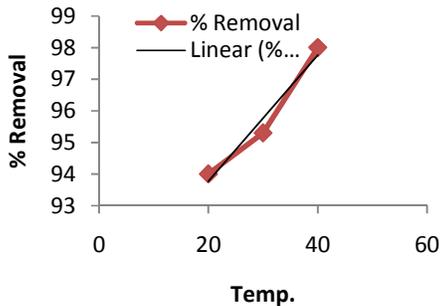


Figure 1 Effect of Temperature on % Removal of Cr VI ion

B. Effect of Solution pH

The pH of the solution is one of the most important parameters affecting the adsorption process since it governs the surface charge of the adsorbent and the chemistry of the metal ions. The effect of pH on the removal of Cr VI ions (30 mg L⁻¹) by the NIO@IFSAC is shown in Figure.2. The percent adsorption of Cr VI ion was observed highest at pH 2.05 which can be explained by the existence of anionic chromate species (CrO₄²⁻, HCrO₄⁻, Cr₂O₇²⁻) in aqueous media which are electro-statically attracted toward the positively charged surface of the nanocomposite at lower pH, while as the pH of

the solution increased over 07 the Chromium ion get precipitated as hydroxides. The results showed that the adsorption process can be used effectively to remove more than 98% Cr VI from acidic effluents (such as electroplating wastes, dyeing, mining etc.), whereas prior pH adjustment is required for neutral or alkaline effluents.

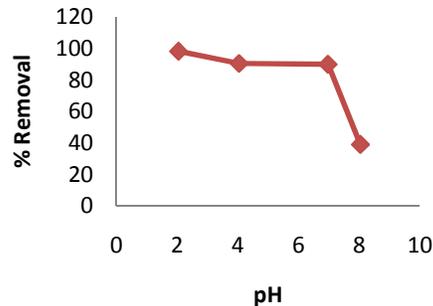


Figure 2 Effect of pH on removal of Cr VI ion

C. Effect of Chromium Concentration

The impact of initial concentrations on the removal of Cr (VI) on NIO@IFSAC adsorbent was studied as shown in Fig.3. The fixed amount of adsorbent is added to 50ml of 05-30ppm aqueous solution of Cr VI and pH of synthetic water at pH 2±05 with stirring (125 RPM) for 20 minutes at 30°C. The figure shows that as the initial metal ion concentration rises, the percentage removal efficiency rises till 30 ppm at reached at 98.2%. At low initial concentrations, sufficient binding sites for Cr(VI) ion adsorption are available; however, at very high effluent concentrations of more than 30 ppm saturation point was observed which can be attributed to the reason that all available binding sites for adsorption have got exhausted, and the percentage removal efficiency of Cr VI ions becomes saturated to maintain equilibrium.

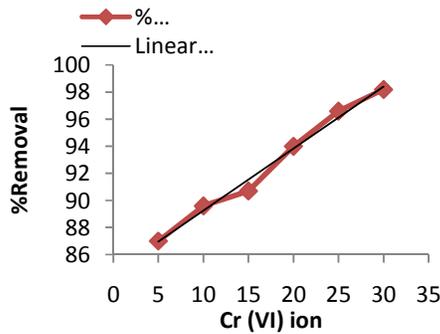


Figure 3 Effect of Initial Concentration of Cr VI ion

D. Effect of Contact Time

The effect of contact time on the uptake of the Cr VI ions ($Cr\ VI\ 30\ mg\ L^{-1}, 30\ ^\circ C, 125\ RPM$) onto NIO@IFSAC was studied by varying the contact time from 10 to 180 min. Figure 4 depicts the amount of metal ions removed by NIO@IFSAC as a function of time. Adsorption of metal ions increases rapidly between 10 to 20 minutes and later on becomes constant when approaching saturation which may be attributed to the availability of least active binding sites with increasing time. Equilibrium was attained within 20 min for Cr (VI) ion adsorption. At equilibrium, the removal percentage for Chromium is found approximately 98%.

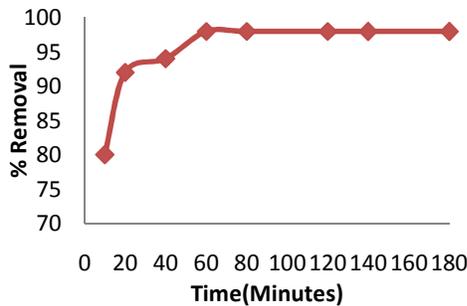


Figure 4 Effect of Contact Time on percentage removal of Cr VI ion

E. Data Analysis and Results:

The synthetic water samples of Chromium (Cr VI) were prepared and agitated with adsorbent at

different set of conditions and the sorption capacity (mg/g) and removal efficiency (% R) was calculated using well known equations-

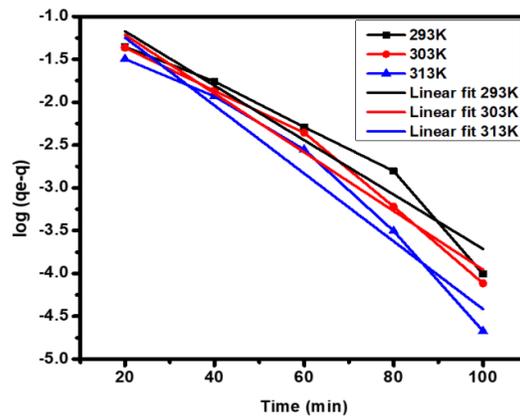
$$Q_e = \frac{(C_i - C_e)V}{m} \dots\dots(1)$$

$$\% \text{Removal efficiency} = \frac{(C_i - C_e)}{C_i} \times 100 \dots\dots(2)$$

Where Q_e is the maximum amount of Chromium (Cr VI) adsorbed (mg/g) on the NIO@IFSAC, C_i and C_e are the initial and final ion concentrations (mg/L) respectively, V is the volume of the medium used (L), and m is the amount of nanocomposite used (g). During this study, Q_e is calculated as 05.90mg/g with 98 % removal efficiency.

F. Kinetic rate constant

The kinetic rate constant (K_{ad}) was determined by using Lagergren's first-order rate expression. The studies of the effect of temperature on adsorption are important because it affects the rate and extent of adsorption and also provides information about adsorbate-adsorbent interaction. The K_{ad} value ($3.63 \times 10^{-2} \text{ min}^{-1}$) at 300C for Cr (VI) removal was calculated from the slopes of the linear plots of $\log (q_e - q_t)$ versus time (t) (Figure 5). The high correlation coefficients ($R^2=0.99$) indicate that adsorption follows first-order rate kinetics.



Figures 5 Adsorption kinetic plots for Cr metal ion removal at different temperatures

Table 2 ADSORPTION KINETIC FOR CR (VI) METAL ION REMOVAL AT DIFFERENT TEMPERATURES

20°C		30°C		40°C	
Time	log(q _e -q _t)	Time	log(q _e -q _t)	Time	log(q _e -q _t)
20	-1.353275	20	-1.364192	20	-1.495196
40	-1.75721	40	-1.86638	40	-1.93188
60	-2.29214	60	-1.86638	60	-2.55415
80	-2.80524	80	-2.35764	80	-3.50393
100	-4.00611	100	-3.22009	100	-4.67205

G. Adsorption Isotherms

To describe the characteristics of adsorbents used in water and wastewater treatment Langmuir and Freundlich isotherms were utilized to depict the equilibrium adsorption. Langmuir isotherm alludes to homogeneous monolayer adsorption whereas the linear form of the Freundlich isotherm model is determined by expecting to be a heterogeneous surface of adsorption limit and adsorption capacity with a nonuniform circulation of heat of adsorption. The equation for linear form of Langmuir isotherm is given by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{(K_L \cdot Q_{max})} + \frac{C_e}{Q_{max}} \dots\dots\dots (3)$$

where q_e is the amount adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration (mg/L), and q_{max}(mg/g) and K_L (L/mg) are the Langmuir constants related to maximum adsorption capacity and K_L adsorption constant, respectively, the plot of C_e/q_e against C_e produced a straightline confirming that the adsorption followed the Langmuir isotherm model. The Langmuir constants for adsorption of Cr (VI) are given in Table 3. The capacity of the NIO@IFSAC for

adsorption of Cr (VI) under the optimized conditions was 05.90mg/g.

The Freundlich isotherm can be expressed as-
 $q_e = K_f C_e^{1/n} \dots\dots\dots (4)$

by rearranging the above equation linear equation can be obtained-

$$\ln q_e = \ln K_f + 1/n \ln C_e (5)$$

where 1/n and K_f are Freundlich constants which correspond to adsorption intensity and adsorption capacity, respectively. The Langmuir and Freundlich adsorption isotherms of Cr (VI) ions onto NIO@IFSAC are given in Table 3.

The table indicated that the values of regression coefficient for Langmuir adsorption were near to unity for Cr(VI) adsorption and values of q_e experimental (5.90 mg/l) and q_e calculated (5.76mg/l) were almost found near to each other thus, revealing that pseudo-first-order model followed during the removal process. Langmuir adsorption model provide better agreement than Freundlich adsorption isotherms as indicated by R² values and experimental results obtained, however chemisorptions cannot be neglected totally .

Table 3 LANGMUIR AND FREUNDLICH ISOTHERMS CONSTANT VALUES FOR ADSORPTION OF CR (VI) IONS ON NIO@IFSAC AT DIFFERENT TEMPERATURES

S.No.	Temperature °C	Langmuir			Freundlich		
		Q _L (mg g ⁻¹)	b (L mg ⁻¹)	R ²	K _F (mg g ⁻¹)	1/n	R ²
1.	20	5.31	0.196	0.9876	0.521	0.799	0.84
2.	30	5.47	0.29	0.9912	0.747	0.794	0.89
3.	40	5.76	0.621	0.9994	1.417	0.807	0.92

IV. CONCLUSIONS

In summary, the present study demonstrates that nanocomposites of Iron Oxide and Ice-apple fruit-shell waste (NIO@IFSAC) can successfully remove Chromium (Cr VI) from aqueous media. The adsorption of Chromium (Cr VI) from aqueous media is significantly affected by pH variation; the optimum conditions for maximum removal efficiency (98%) for Chromium (Cr VI) was found to be at pH2.05 with adsorption capacity of NIO@IFSAC being 05.90 mg/g. The present research work proves that the waste materials like Ice-apple fruit shells (IFS) can be converted in nanocomposite and used as cost-effective nanosorbent for Chromium (VI) ion contaminant effluent treatment.

Conflict of interest

The authors declare no conflict of interests.

REFERENCES

- Dyg, S., Cornelis, R., Griepink, B., Verbeeck, P. (1990). Stability Study of Cr (III) and Cr(VI) in Water for Production of an Aqueous Chromium Reference Material. In: Broekaert, J.A.C., Güçer, Ş., Adams, F. (eds) Metal Speciation in the Environment. NATO ASI Series, vol 23. Springer, Berlin, Heidelberg. https://link.springer.com/chapter/10.1007/978-3-642-74206-4_19#citeas
- DeLoughery, Z., Luczak, M. W., & Zhitkovich, A. (2014). Monitoring Cr intermediates and reactive oxygen species with fluorescent probes during chromate reduction. *Chemical research in toxicology*, 27(5), 843–851. <https://doi.org/10.1021/tx500028x>
- Jeroen Buters, TiloBiedermann, Chromium(VI) Contact Dermatitis: Getting Closer to Understanding the Underlying Mechanisms of Toxicity and Sensitization!, *Journal of Investigative Dermatology*, Volume 137, Issue 2, 2017, Pages 274-277, <https://doi.org/10.1016/j.jid.2016.11.015>
- Helena Oliveira, "Chromium as an Environmental Pollutant: Insights on Induced Plant Toxicity", *Journal of Botany*, vol. 2012, Article ID 375843, 8 pages, 2012. <https://doi.org/10.1155/2012/375843>
- Bakshi, A., & Panigrahi, A. K. (2018). A comprehensive review on chromium induced alterations in fresh water fishes. *Toxicology reports*, 5, 440–447. <https://doi.org/10.1016/j.toxrep.2018.03.007>
- Cheng Tan, SumantAvasarala, and Haizhou Liu, *Environmental Science & Technology* 2020 54 (20), 13036-13045, <https://doi.org/10.1021/acs.est.0c03922>
- Jessica Briffa, Emmanuel Sinagra, Renald Blundell, Heavy metal pollution in the environment and their toxicological effects on humans, *Heliyon*, Volume 6, Issue 9, 2020, e04691, <https://doi.org/10.1016/j.heliyon.2020.e04691>
- https://cdn.who.int/media/docs/default-source/wash-documents/wash-chemicals/chromium_history.pdf?sfvrsn=971a14cb_5#:~:text=In%20a%20background%20document%20for,effects%20associated%20with%20hexavalent%20chromium.
- Joel Brian Njewa, Ephraim Vunain, Timothy Biswick, "Synthesis and Characterization of Activated Carbons Prepared from Agro-Wastes by Chemical Activation", *Journal of*

- Chemistry, vol. 2022, Article ID 9975444, 13 pages, 2022. <https://doi.org/10.1155/2022/9975444>
- 10 Saleem, J., Shahid, U., Hijab, M. et al. Production and applications of activated carbons as adsorbents from olive stones. *Biomass Conv. Bioref.* 9, 775–802 (2019). <https://doi.org/10.1007/s13399-019-00473-7>
- 11 Couto, G. M., Dessimoni, A. L. D. A., Bianchi, M. L., Perígolo, D. M., & Trugilho, P. F. (2012). Use of sawdust Eucalyptus sp. in the preparation of activated carbons. *Ciência e Agrotecnologia*, 36, 69-77. <https://doi.org/10.1590/S1413-70542012000100009>
- 12 Allwar Allwar, Retno Hartati, and Is Fatimah, "Effect of nitric acid treatment on activated carbon derived from oil palm shell", AIP Conference Proceedings 1823, 020129 (2017). <https://doi.org/10.1063/1.4978202>
- 13 Xiaolan Song, Ying Zhang, and Caimin Chang, *Industrial & Engineering Chemistry Research* 2012 51 (46), 15075-15081, <https://doi.org/10.1021/ie3012853>
- 14 Harris, P. J., Liu, Z., & Suenaga, K. (2010, July). Imaging the structure of activated carbon using aberration corrected TEM. In *Journal of Physics: Conference Series* (Vol. 241, No. 1, p. 012050). IOP Publishing. <http://dx.doi.org/10.1088/1742-6596/241/1/012050>
- 15 Yoshizawa, N., Ma ruyama, K., Yamada, Y., & Zielinska-Blajet, M. (2000). XRD evaluation of CO₂ activation process of coal- and coconut shell-based carbons. *Fuel*, 79(12), 1461-1466 <https://doi.org/10.1016/S0016-2361%2800%2900011-9>
- 16 Bergna, D., Hu, T., Prokkola, H. et al. Effect of Some Process Parameters on the Main Properties of Activated Carbon Produced from Peat in a Lab-Scale Process. *Waste Biomass Valor* 11, 2837–2848 (2020). <https://doi.org/10.1007/s12649-019-00584-2>
- 17 Williams, P. T., & Reed, A. R. (2006). Development of activated carbon pore structure via physical and chemical activation of biomass fibre waste. *Biomass and bioenergy*, 30(2), 144-152. <http://dx.doi.org/10.1016/j.biombioe.2005.11.006>
- 18 Lillo-Ródenas, M. A., Cazorla-Amorós, D., & Linares-Solano, A. (2003). Understanding chemical reactions between carbons and NaOH and KOH: an insight into the chemical activation mechanism. *Carbon*, 41(2), 267-275. <https://doi.org/10.1016/S0008-6223%2802%2900279-8>
- 19 Guo, Y., & Rockstraw, D. A. (2006). Physical and chemical properties of carbons synthesized from xylan, cellulose, and Kraft lignin by H₃PO₄ activation. *Carbon*, 44(8), 1464-1475.
- 20 Joseph Jjagwe, Peter Wilberforce Olupot, Emmanuel Menya, Herbert Mpagi Kalibbala, Synthesis and Application of Granular Activated Carbon from Biomass Waste Materials for Water Treatment: A Review, *Journal of Bioresources and Bioproducts*, 6-4, 2021, 292-322, <https://doi.org/10.1016/j.jobab.2021.03.003>.
- 21 Stavropoulos, G. G., & Zabaniotou, A. A. (2005). Production and characterization of activated carbons from olive-seed waste residue. *Microporous and Mesoporous Materials*, 82(1-2), 79-85.
- 22 Ash, B., Satapathy, D., Mukherjee, P. S., Nanda, B., Gumaste, J. L., & Mishra, B. K. (2006). Characterization and application of activated carbon prepared from waste coir pith.
- 23 Yagmur, E., Gokce, Y., Tekin, S., Semerci, N. I., & Aktas, Z. (2020). Characteristics and comparison of activated carbons prepared from oleaster (*Elaeagnus angustifolia* L.) fruit using KOH and ZnCl₂. *Fuel*, 267, 117232.
- 24 Bansal, R. C., Donnet, J. B., & Stoeckli, F. (1988). *Active Carbon*, Marcel Decker. Inc., New York, 482.
- 25 Saka, C. (2012). BET, TG–DTG, FT-IR, SEM, iodine number analysis and preparation of activated carbon from acorn shell by chemical activation with ZnCl₂. *Journal of Analytical and Applied Pyrolysis*, 95, 21-24, <http://dx.doi.org/10.1016/j.jaap.2011.12.020>
- 26 Vunain, E., Kenneth, D. & Biswick, T. Synthesis and characterization of low-cost activated carbon prepared from Malawian baobab fruit shells by H₃PO₄ activation for removal of Cu(II) ions: equilibrium and kinetics studies. *Appl Water Sci* 7, 4301–4319 (2017). <https://doi.org/10.1007/s13201-017-0573-x>
- 27 Hoang Thu Ha, Pham Tuan Phong, Tran Dinh Minh, "Synthesis of Iron Oxide Nanoparticle Functionalized Activated Carbon and Its Applications in Arsenic Adsorption", *Journal of Analytical Methods in Chemistry*, 2021, 9 pages, 2021. <https://doi.org/10.1155/2021/6668490>