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Amputation of Hexavalent Chromium [Cr (Vi)] from Aqueous Medium by H_3PO_4 Activated *Aerva lanata* Stem Carbon: Adsorption Dynamics and Equilibrium Studies

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ABSTRACT

This study aims to explore the mechanism of Cr^{6+}reduction (removal) in aqueous solutions using an adsorbent, specifically activated carbon (adsorbent) derived from *Aerva lanata* stems. Through treatment with H_3PO_4, activated carbon, known as PAALC, was obtained. Batch experiments were conducted to assess the influence of various factors such as pH, dosage, contact time, initial ion concentration, and temperature. The findings indicated that the initial adsorption of Cr^{6+}ions onto PAALC conforms well to the Langmuir isotherm model. Kinetic analysis revealed that the pseudo-second-order model best describes the equilibrium data, suggesting a rapid rate of Cr^{6+}ion adsorption. Moreover, the study underscores the substantial potential of PAALC in effectively removing Cr^{6+} from water.

Key words: *Hexavalent Chromium Ion, Phosphoric Acid, Aerva lanata, Adsorption.*

Introduction

Discharge of industrial effluent that poses a threat of polluting water with toxic heavy metals is a world-wide issue (Rafatullah *et al*., 2012). Sb, Cr^{6+}, Cd, Cu, Pb, Hg, and other metals are hazardous to the environment and humans (Taty-Costodess *et al*., 2003). Chromium is one of the heavy elements mentioned earlier and is also one of the important elements that are found in the existence as well as the health of human beings. While the human body requires a small amount of metal to stay healthy, large amounts of it cause cancer. Cr^{6+} is toxic and causes severe health effects in humans when one is exposed to it for a long time (Yu *et al*., 2000). According to the WHO, the allowable concentration of this element in external water remains is 0.05 mg/l. In industrial wastewater, the concentration ranges from 0.5 to 270 mg/L. The industries that use photography include Lather, tanning, pigment, textiles, wood preservation, cement, chrome plating, and photography. Thus, it becomes important to treat water that has been labeled as tainted. Among the methods used in the present times for the management of developed wastewater are "chemical precipitation", "membrane separations", "Ion exchange", "solvent extraction", 'adsorption", 'electrodialysis', and "reverse osmosis. Among these highly efficient methods, one must mention the adsorption one as it is relatively cheap since it uses cheap adsorbents. There is a great

[b]Principal (Retd)

potential for raising efficiency, assisting in environmental regeneration, and reducing such environmental challenges (Kadievelu *et al*., 2001).

Some of the low-cost adsorbents include biomass, clay minerals, industrial solid wastes, agricultural wastes, and zeolites for the removal of Cr^{6+} (Rangabhashiyam *et al*., 2014). Activated carbon (AC) is a very efficient and environmentally friendly adsorbent because of its large sorption capacity, many surfaces functional groups, and low specific area (Rai *et al*., 2016). A stem of *Aerva lanata* activated by phosphoric acid-activated carbon (PAALC) was synthesized and used in the removal of Cr^{6+}ions from an aqueous solution (Kiruthiga *et al.*, 2021). In this work, the experimental parameters affecting the adsorption were analyzed. Other analyses that were conducted include kinetics experiments and adsorption isotherms. The findings reveal that PAALC is cheap for amputations and can be used as an absorbent.

Methodology

Activation of carbon

The stems of *Aerva lanata* were assembled in the Trichy region. They were often rinsed with distilled water to reduce the presence of dust and other impurities. They were then left to dry for a week in the sun for them to harden. To ensure that the H_3PO_4 could reach *Aerva lanata* stem, 20g of the dried and chopped material was dipped in 60 ml of 60 % H_3PO_4. Subsequently, the slurry was heated in a microwave for 10 min at a power of 850 W. The carbon produced through the described procedure was washed with diluted. HCl, followed by both warm and cold distilled water. Afterward, the carbon was sieved, dried in an oven at 423 K, and stored in a desiccator for future use (Ramesh *et al*., 2014; Namasivayam *et al*., 2004).

Adsorbate Solution Preparation

In the case of all the compounds, no additional purification was performed, and all the compounds were used during the studies as obtained in analytical grade from the supplier. For all the trials, distilled water is used, and it is further distilled once before use.

One liter volume was used to dissolve to prepare Cr^{6+}at a concentration of one thousand mg per liter 828 g of potassium dichromate were used to create a stock solution.

Batch Adsorption Experiments

In this study, the removal of Cr^{6+}ions by PAALC were investigated using the batch method at three different temperatures (305K, 315K, and 325K) to examine the impact of various operational parameters, including initial ion concentration, contact time, adsorbent dosage, pH, and temperature. This approach involves adjusting one variable at a time while keeping the others constant. Three predetermined initial ion concentrations were tested. The experiments were conducted using 250 milliliter iodine flasks, each containing one gram of the adsorbent and 50 ml of the ion solution. The mixture was agitated at 140 rpm in a rotary shaker for the required duration. After centrifuging the samples, a Systronics double-beam UV-visible spectrophotometer (model number: 2202) was employed to measure the OD value. The percentage of ion removal was calculated using the following formula (Zein *et al*., 2015; Abu-El-Halawa *et al*., 2016).

$$\text{Removal (\%)} = C_i\text{-}C_t / C_i \times 100 \quad \ldots\ldots\ldots\ldots 2.1$$

Nomenclature

C_i	Initial concentrations of the adsorbate in the liquid phase (mg/L)
C_t	Concentrations of the adsorbate in the liquid phase at time "t" (mg/L)
C_e	Concentrations of the adsorbate in the liquid phase at equilibrium (mg/L)
C_e	Equilibrium concentration of solute in the bulk solution (mg/L)
C_0	The initial concentration of the adsorbate
B	Langmuir adsorption energy
q_t	Quantity of adsorbate adsorbed at time "t" (mg/g)
qe	Quantity of adsorbate adsorbed at equilibrium (mg/g)
h	Initial adsorption rate (mg/g min)
k_1	The rate constant of adsorption (1/min)
k_2	Second-order constants
K_f and n	Freundlich constants, adsorption capacity and intensity, respectively
Q_e	Amount of solute adsorbed per unit weight of adsorbent (mg/g)
Q0	Langmuir adsorption efficiency
RL	Langmuir separation factor
N	Number of data points
V	The volume of Chromium solution in a liter (L)

Tools for Data Analysis

No.	Limits	Formula
1.	**Kinetics Sum of error squares %**	
	"Pseudo First-Order Kinetics (Lagergren Equation)" (Lagergren, 1898)	$\log (q_c - q_t) = \log q_c - \frac{k_1}{2.303} \times t$
	"Pseudo Second-Order Kinetics (Ho Equation) "(Ho, 1999)	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$
	"Initial Adsorption Rate"	$h = k_2 q_e^2$
	"The sum of Error Squares (SSE) " (Mittal *et al*., 2010)	$SSE(\%) = V\sum \left[(q_{exp} - q_{cal})^2\right]/N$
2.	**Isotherms**	
	"Langmuir" (Fethi Kooli *et al*., 2015)	$\frac{C_d}{Q_c} = \frac{1}{Q_0 b} + \frac{C_d}{Q_0}$
	'Separation Factor"	$R_L = \frac{1}{1 + bC_0}$
	"Freundlich" (Freundlich, 1906)	$\log Q_e = \log K_f + \frac{1}{n} \log C_e$

W Mass of the adsorbent (g)
T Time in minutes

Results and Analysis

The impact of adsorbent dosage on dye adsorption from the solution was examined to assess its significance. Specifically, the research concentrated on the adsorption of Cr^{6+}ions using PAALC, with an initial Cr^{6+}ion concentration of 50 mg/l and adsorbent dosages range from 10 mg/50 ml to 100 mg/50 ml. The findings revealed that the removal efficiency of Cr^{6+}ions from the aqueous solution improved as the carbon dosage increased. This enhancement is attributed to the greater number of adsorption sites and the expanded surface area of the carbon adsorbent. (Wassie *et al*., 2016). The results are illustrated in Fig. 1.

Impact of pH

Figure 2 illustrates the influence of solution pH on the adsorption behavior of Cr^{6+} onto the prepared adsorbent. The results indicate that PAALC exhibited maximum adsorption of Cr^{6+} ions at a pH of 2.0. Interestingly, as the pH increased, the adsorption efficiency also increased. This trend can be attributed to the decrease in the net positive surface charge, leading to a weakening of the electrostatic attraction between the adsorbent and the Cr^{6+} ions with rising pH levels (Usman Khalil *et al*., 2021).

Consequence of Contact Time

The third factor is Contact time Contact time is the time spent with the source or with an agent that has been in contact with the source.

The result of the contact period on the quantity of Cr6+ion that was removed from the "aqueous solution" is presented in Figure 3. The adsorbate was rapidly taken up during the first stages of the adsorption process as noted by other authors (Demirbas *et al*., 2004). The efficiency of the exclu-

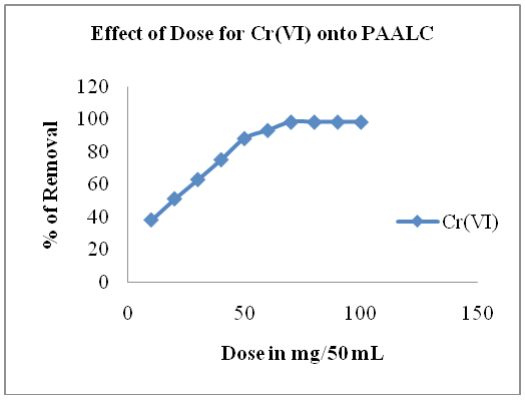

Fig. 1

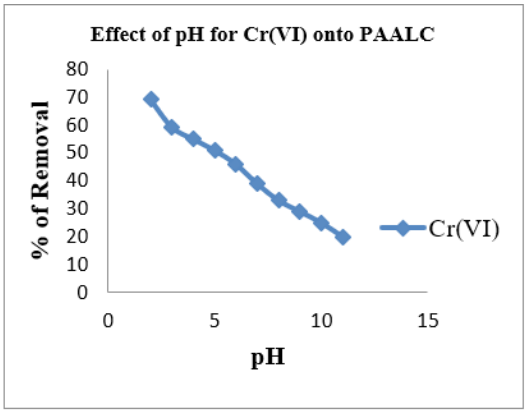

Fig. 2.

sion of the Cr6+ ion increases sharply till it attains an optimum level after which the increase is gradual and slow. This is because at the beginning of adsorption, many surface sites are available for adsorption but as the process continues the available surface sites decrease. Finally, after eighty minutes there was no considerable amendment in the adsorption % of the dye by the treated coconut copra fiber.

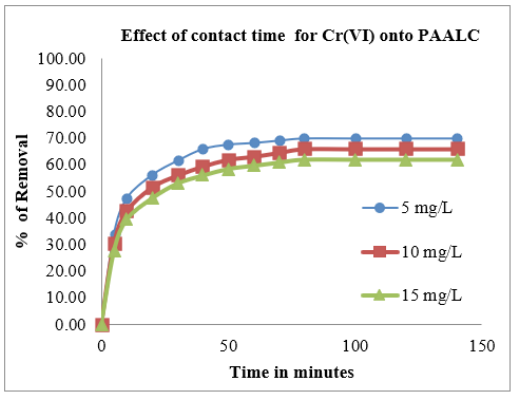

Fig. 3

Effect of Initial Concentration

Figure 4 demonstrates that, as discussed in section 4, the fraction of residual Cr^{6+}ions reduces with a rise in the primary concentration of Cr^{6+}ions across all temperatures studied. This is because the adsorption sites on the adsorbent become occupied, making further adsorption less efficient even when the concentration of the adsorbate is increased (Razmovski *et al*., 2008).

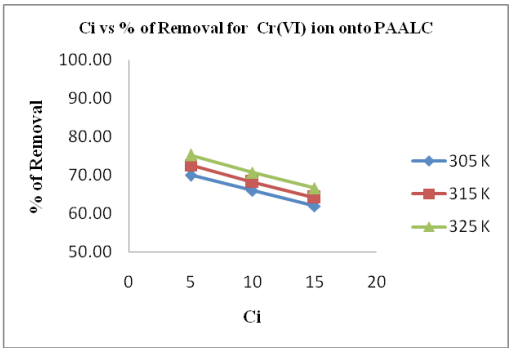

Fig. 4

Effect of Temperature

Temperature is a limiting factor that significantly affects the adsorption processes. The elimination of metal ions accelerates from 305, 315, and 325K. The results are depicted in Figure 5 and suggest that the adsorption process was more affected by the experimental temperature since higher temperatures gave higher surface coverage. This phenomenon may stem from the emergence of fresh active sites at elevated temperatures or the heightened infiltration of metal ions into smaller pores (Ramesh *et al*., 2014).

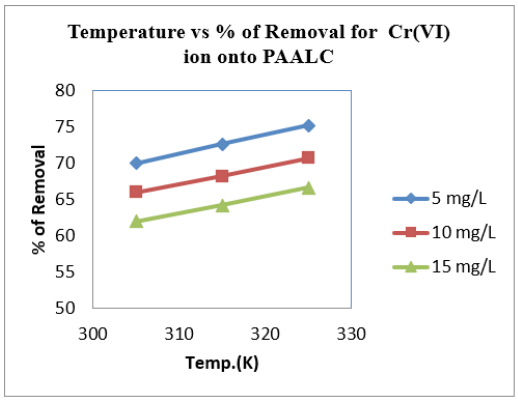

Fig. 5

Adsorption Isotherm

The Langmuir isotherm analysis conducted in this study reveals that as temperature increases, there is a notable rise in adsorption energy and carbon's adsorption capacity. Calculated values indicate relatively low sorption energy but increased adsorption efficiency with temperature elevation. RL values confirm favorable adsorption conditions, while 'n' values within the favorable range suggest varied adsorption mechanisms. The increase in 'n' values with temperature signifies strengthened adsorbent-adsorbate interaction, supported by higher Kf values. These findings highlight PAALC's efficacy in Cr^{6+}removal across temperatures, contributing to understanding adsorption processes and guiding remediation strategies for Cr^{6+}pollution. The plots illustrating Langmuir and Freundlich isotherms are included in Table 1 and Figures 6 (A) and 6 (B), respectively.

Adsorption Kinetics

The rate of absorption was also studied. The reac-

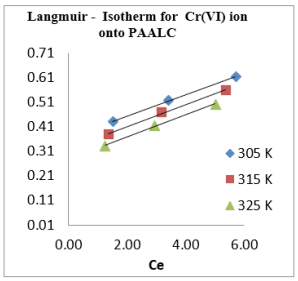

Fig. 6(a)

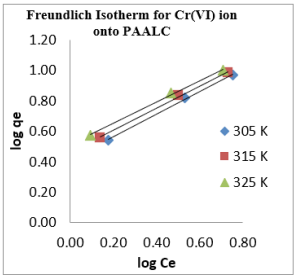

Fig. 6(b)

Table 1. Results of "Langmuir & Freundlich isotherm" plot for the adsorption of Cr^{6+}onto PAALC

	"Langmuir isotherm"				"Freundlich isotherm"		
Temp(K)	Q_0(mg/g)	b (L/mg)	R^2	R_L 5mg/L	n	kf	R^2
305	22.222	0.118	0.999	0.6286	1.4451	2.6182	0.9980
315	22.727	0.138	0.997	0.5910	1.3947	2.9174	0.9980
325	23.256	0.163	0.997	0.5509	1.3605	3.2659	0.9980

Table 2. Modeling Cr6+Adsorption onto PAALC: Exploring "Pseudo-first order" and "Pseudo-second order"Kinetics

Model /Limitations	Cr6+			
"Pseudo first order"	5 mg/l	10 mg/l	15 mg/l	MSSE
K_1 (min^{-1})	0.0576	0.0461	0.0484	
qe(exp) (mg/g)	3.50	6.60	9.30	1.46
qe(cal) (mg/g)	2.2699	3.9994	5.9841	
R^2	0.990	0.991	0.994	
"Pseudo-second order"	5 mg/l	10 mg/l	15 mg/l	MSSE
K_2 (g $mg^{-1}min^{-1}$)	0.0661	0.0279	0.0191	
qe(cal) (mg/g)	3.65	6.90	9.80	0.20
R^2	0.998	0.997	0.997	

tion kinetics of the activity were acquired to be "pseudo-second order" as depicted in Table 2 and Figure. 7(A) and 7(B) because its R^2 value is 0. 998, while the R^2 of pseudo first order kinetics is 0. 990. (B). The assessment of adsorption kinetics is very important in understanding the rate of adsorption and the required time for equilibrium (Ganesapillai *et al*., 2015).

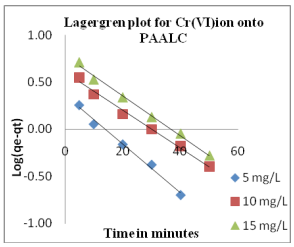

Fig. 7(a)

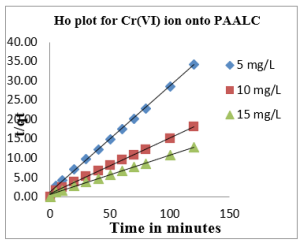

Fig. 7(b)

Several variables of each model were derived using the slope and y-intercept of an appropriate linear regression line. Figures 3.7(A) and 3. 7 give instances of (B).

Furthermore, it was observed that the trend of the obtained experimental qe values was nearly identical to that of the theoretical qe values in this study. Table 1 provides the MSSE values as a kinetic tool. Therefore, the lower MSSE value of the "pseudo-second-order kinetic" models indicates the best kinetic model for the selected adsorption process (Sattar *et al*., 2019).

Conclusion

PAALC, derived from *Aerva lanata* stems through phosphoric acid activation, emerges as a confirming solution for the exclusion of $Cr^{6+}$from water solutions. Through meticulous batch processes, the study examined various parameters to understand their influence on Cr^{6+} reduction. Notably, the investigation uncovered a direct relationship between contact time and adsorbent quantity with the adsorption capacity, shedding light on the intricate dynamics governing the process.

A pivotal finding of the study was the attainment of maximum removal efficiency within 80 minutes of experimentation, underscoring the efficacy of PAALC in rapid and efficient chromium removal. Further analysis using Langmuir and Freundlich adsorption isotherms provided deeper insights into the adsorption mechanism. The Langmuir model's confirmation of effective metal adsorption in a monolayer configuration, alongside the favorable Langmuir RL values, suggests an optimal adsorption environment. Similarly, the Freundlich isotherm's n value, indicating favorable adsorption, further validates PAALC's efficacy.

Additionally, the adoption of a "pseudo-second order" kinetic model showed the efficient adsorption kinetics of the process, reinforcing the practical applicability of PAALC in chromium removal applications. Collectively, these findings not only under-

score the cost-effectiveness of PAALC but also highlight its potential as an efficient and sustainable solution for hexavalent chromium removal, thereby addressing critical environmental and public health concerns associated with chromium contamination.

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Conflict of Interest

The author declare no conflict of interest

References

Abu-El-Halawa, R.,Zabin, S. and Abu-Sittah, H. 2016. Investigation of Methylene Blue Dye Adsorption from Polluted Water Using Oleander Plant (Al Defla) Tissues as Sorbent. *Am. J. Environ. Sci.* 12: 213-224.

Demirbas, E., Kobya, M., Senturk, E. and Ozkan, T. 2004. Adsorption kinetics for the removal of chromium (VI) from aqueous solutions on the activated carbons prepared from agricultural wastes. *Water SA.* 30(4): 533 -539.

Fethi Kooli, Liu Yan, Rawan Al-Faze and Awadh Al-Sehimi, 2015. Removal enhancement of basic blue 41by brick waste from an aqueous solution. *Arabian Journal of Chemistry*. 8: 333-342.

Freundlich, H.M.F. 1906. Over the Adsorption in Solution. *J. Phys. Chem*. 57: 385-471.

Ganesapillai, M. and Simha, P. 2015. The rationale for alternative fertilization: equilibrium isotherm, kinetics and mass transfer analysis for urea-nitrogen adsorption from cow urine. *Resour. Effic. Technol*. 1: 90-97.

Ho, Y.S. and McKay, G. 1999. Pseudo-second order model for sorption processes. *Process Biochem.* 34:451-465.

Kadievelu, K., Thamaraiselvi, K. and Namasivayam, C. 2001. Removal of heavy metals from industrial wastewaters by adsorption onto activated carbon prepared from an agricultural solid waste. *Biores Technol.* 76: 63-65.

Kiruthiga, M., Ramesh, K., Rajappa, A. and Kammalakannan, S. 2021. Adsorptive remediation of Chromium (VI) and Copper (II) ions onto Microwave Assisted Phosphoric Acid Activated Carbon prepared from aerial root of *Ficus benghalensis* L. *Journal of Advanced Scientific Research.* 12(2): 196-204.

Lagergren, S. 1898. About the Theory of so Called Adsorption of Soluble Substances, Kungliga Svenska Vetenskapsakademiens Handlingar. 24: 1-39.

Mittal, A., Mittal, J., Malviya, A., Kaur, D. and Gupta, V.K. 2010. Adsorption of hazardous dye crystal violet from wastewater by waste materials. *J. Colloid Interface Science.* 343(2): 463- 473.

Namasivayam, C. and Sangeetha, D. 2004. Equilibrium and kinetic studies of adsorption of phosphate onto ZnCl2 activated coir pith carbon. *J. Colloid and Interface Science.* 280: 359-365.

Rafatullah, M., Sulaiman, O., Hashim. R. and Ahmed, A. 2012. Removal of cadmium(II) from aqueous solutions by adsorption using meranti wood. *Wood Sci Technol.* 46: 221-241.

Rai, M.K., Shahi, G., Meena, V., Meena, R., Chakraborty, S., Singh, R.S. and Rai, B.N. 2016. Removal of hexavalent chromium Cr (VI) using activated carbon prepared from mango kernel activated with H3PO4. *Resource-Efficient Technologies*. 2: S63-S70.

Ramesh, K., Rajappa, A. and Nandhakumar, V. 2014. Kinetics of Adsorption of Methylene Blue onto Microwave Assisted Zinc Chloride Activated Carbon Prepared from Delonixregia pods. *International Journal of Chemistry and Pharmaceutical Sciences*. 2(8): 878-885.

Ramesh, K., Rajappa, A. and Nandhakumar, V. 2014. Adsorption of Hexavalent Chromium onto Microwave Assisted Zinc Chloride Activated Carbon Prepared from *Delonixregia* Pods. *International Journal of Research in Chemistry and Environment*. 4(3): 1-9.

Rangabhashiyam, S., Anu, N. and Selvaraju, N. 2014. Equilibrium and kinetic modeling of chromium (VI) removal from aqueous solution by a novel biosorbent. *Res. J. Chem. Environ.* 18: 30-36.

Razmovski, R. and Sciban, M. 2008. Biosorption of Cr(VI) and Cu(II) by waste tea fungal biomass. *Ecol. Eng*. 34: 179-186.

Sattar, M.S., Shakoor, M.B., Ali, S. and Rizwan, M. 2019. Comparative efficiency of peanut shell and peanut shell biochar for removal of arsenic from water. *Environ Sci Pollut Res*. 26: 18624-18635.

Taty-Costodess, V.C., Fauduet, H., Porte, C. and Delacroixs, A. 2003. Removal of Cd(II) and P(II) ions from aqueous solutions by adsorption onto sawdust of pinussylvestris. *J Hazard Mater.* 105: 121-142.

Usman Khalil, Muhammad Bilal Shakoor and Shafaqat Ali, 2021. Selective Removal of Hexavalent Chromium from Wastewater by Rice Husk: Kinetic, Isotherm and Spectroscopic Investigation. *Water*. 13:163.

Wassie, A.B. and Srivastava, V.C. 2016.Chemical treatment of teff straw by sodium hydroxide, phosphoric acid and zinc chloride: adsorptive removal of chromium. *Int. J. Environ Sci. Technology.* 13: 2415-2426.

Yu, B., Zhang, Y., Shukla, A., Shukla, S.S. and Dorris, K.L. 2000. The removal of heavy metal from aqueous solutions by sawdust adsorption - removal of copper. *J Hazard Mater.* 80: 33-42.

Zein, R., Astuti, A.W., Wahyuni, D., Furciani, F. and Khoiriah, Munaf, E. 2015. Removal of Methyl Red from Aqueous Solution by *Neplhelium lappaceum*. *Res. J. Pharm. Biol. Chem. Sci.* 3: 86-97.