REMOVAL OF HEXAVALENT CHROMIUM FROM TANNERY WASTE WATER BY ADSORPTION ON THE ACTIVATED CARBON SYNTHESIZED FROM GROUNDNUT FOLIAGE & HUSK (ARACHIS HYPOGAEA)

Section A-Research paper

REMOVAL OF HEXAVALENT CHROMIUM FROM TANNERY WASTE WATER BY ADSORPTION ON THE ACTIVATED CARBON SYNTHESIZED FROM GROUNDNUT FOLIAGE & HUSK (ARACHIS HYPOGAEA)

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ABSTRACT

Since hexavalent chromium is one of the major pollutants released from the tanneries that have a direct effect on man and animals. In this study reports adsorption of hexavalent chromium (Cr (VI)) ions from tannery waste water collected from tannery industrial region using activated carbon prepared from Groundnut plant. The sample of impregnated Groundnut stem and Groundnut (Arachis hypogaea) stem were activated in muffle furnace at 650 -700°C respectively for 90 minutes then cooled at room temperature. Various adsorption characteristics such as dose of the adsorbent, agitation time, initial Cr (VI) ion concentration, pH of the solution and temperature on adsorption were studied for removal of Cr (VI) ions from aqueous solution by batch mode. Also the equilibrium adsorption was analyzed by the Langmuir, Freundlich, Tempkin and D-R isotherm models. The order of best describing isotherms was given based on R^2 value. The pseudo second-order kinetic model best fitted with the Cr (VI) adsorption data. Thermodynamic parameters were also determined and results suggest that the adsorption process is a spontaneous, endothermic and proceeded with increased randomness.

Key words: Hexavalent chromium, Tannery waste water, Activated carbon, Groundnut

1. INTRODUCTION

The industrial effluents discharges in surface and groundwater is a serious environment problem. The industrial effluent contains large amount of chemical components like chloride, phosphate, nitrate, sulphate and heavy metal etc., which is difficult to remove from groundwater and waste water. The activated carbon used to remove the pollutants from waste water by adsorption method. It is one of the important methods to treat the industrial wastewater [1-5]. Exposure to hexavalent chromium can induce allergies, irritations, eczema, and ulceration, nasal and skin irritations, perforation of eardrum, respiratory track disorders and

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lung carcinoma. Also, Cr (VI) evidences the capability of accumulating in the placenta, damaging fetal development. Cr (VI) pollution in the environment changes the structure of soil microbial communities, reducing microbial growth and related enzymatic activities, with a consequent persistence of organic matter in soils and accumulation of Cr (VI). The toxic action of Cr (VI) is due to its capability to easily permeate into cellular membranes, and cell membrane damages caused by oxidative stress induced by Cr (VI) have been extensively reported, both in eukaryotic and prokaryotic cells. It is a very dangerous chemical form on biological systems as it can induce mutagenic, carcinogenic and teratogenic effects. Moreover, Cr (VI) is able to induce oxidative stress in cells, damaging its DNA. Considering the dangerous effects Cr (VI) can cause to human health, Cr (VI) has been consisted of among the priority pollutants and listed as a class A human carcinogen by the US Environmental Protection Agency [6-11].

These techniques have a few disadvantages, such as a particularly high amount of sludge disposal, the development of large-sized particles, blockage of membranes by metal hydroxide formation, and high operation costs. Hence, adsorption is considered an economical method because of its simple design, and a wide assortment of efficient adsorbents has been accounted for [12 & 13]. Activated carbon is a remarkable adsorbent of pollutants in water [14]. It is a black solid (homogeneous or heterogeneous surface), either pelletized or microcrystalline, with a large surface area and high porosity [15]. Commercially available activated carbon is extremely expensive; hence, activated carbon prepared from low cost materials (such as groundnut shell, rice husk, sawdust, bark and stems of plants) could profoundly reduce the expense of the Cr (VI) adsorption process [16-20].

The jack fruit peel activated carbon is used to remove the dye of malachite green from industrial waste. The activated carbon of agricultural waste is used to remove the dye of methylene blue from waste water [21]. The thespesiapopulnea activated carbon is used to remove the orange G dye from aqueous solution by adsorption method. Activated carbon adsorption is one of the great potential methods for the removal of dyes from wastewater [22-30]. The different shape of activated carbons is synthesized and used in adsorption process such as granular activated carbon and powdered activated carbon. The adsorption was analyzed by Freundlich's adsorption isotherm for water and waste water treated by activated carbon due to high rate and capacity [31-34].

In this study, waste water from leather industries which is drained into tannery industrial region located at Ranipet taluk without treatment was collected and treated with algal extracts. Tannery effluents are characterized as high-coloured, foul-smelling, acidic, and alkaline liquor. The disposals of these effluents into any surface water are affecting its quality in diverse ways. The high organic content interferes with the oxygen content of the receiving water [35 - 38]. Presence of lime, short hair, fleshing, etc., makes the water cloudy, and the colouring substance alters the taste and odour. The various strategies (Fig 1) have been addressed for the expulsion of Cr (VI) from contaminated water and procedures, such as precipitation, electro-dialysis, electro de-fluoridation, membrane, filtration, ion-exchange, oxidation, coagulation and reverse osmosis, etc., are utilized [38–46].

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2 MATERIALS AND METHODS

Activated carbon from groundnut foliage and groundnut husk is used in this experiment. The groundwater samples were collected from bore wells located in residential areas of Cuddalore district using clean polythene bottles and it is preserved in refrigerator. The samples were analyzed according to world health organization and ISI standard. The double distilled water is used to prepare the all reagents [46-50].

Collection of effluent:

Tannery wastewater was collected from the canal which was nearby tanneries located areas of Ranipet taluk, Tamil Nadu and was preserved in a refrigerator to avoid further microbial contamination.

Preparation of algal extracts:

Collected water samples were soaked in different solvents such as methanol, ethanol, water, chloroform and benzene. Then the extracts were collected.

Phytochemical analysis:

Phytochemical analysis of extracts was done by standard methods. Treatment of effluent: 10 mL of algal extract was added to 100 mL of effluent and was left for 5 days. After five days of treatment, concentration of hexavalent chromium was analysed.

Estimation of Cr (VI) concentration:

Concentration of Cr (VI) was analysed by using APHA (1998)

Activated Carbon

The sample of impregnated groundnut foliage and husk were activated in muffle furnace at 650 -700°C respectively for 90 minutes then cooled at room temperature. The cold water, acid or base used to wash the activated sample then followed by distilled water used to remove the excess chemical agent. The washed samples were dried in oven at 80 ±5°c for 24 hours. The air tight polyethylene bag used to keep the final activated samples. The scanning electron microscope (SEM) used to analyze its morphology [51-53].

Figure 1: Arachis Hypogaea (Groundnut)]

Adsorptions of Contaminants

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The study of adsorption equilibrium was carried out by using granular activated carbon, produced of mass 3, 5, 7and 9 g. Each mass was placed in 250 ml of Erlenmeyer flask contains 100 ml of waste water. Each flask was shaken continuously for 3 hours. The percolation of activated carbon with effluent of waste water until equilibrium was achieved. After 5 minutes interval the mixture was taken and filtered, the determination of Cr (VI) content in filtrate. To achieved removal of organic compounds by varying dosages of activated carbon as well as solid fluid phase equilibrium type. The data of equilibrium obtained, processed adsorption of contaminated in activated carbon using Langmuir and Freundlich's adsorption isotherm, which are commonly used in waste water and water treatment [54].

Table 1: Classical method of prepared activated carbon

Biomass	Reagent	Impregnation Ratio	Temp (°C)	Impregnation Time (h)	Activation Time (h)
Groundnut foliage and husk	KOH	1:1	690±10	22±2	1
	ZnCl$_2$	1:2	690±10	22±2	1
	H$_3$PO$_4$	1:3	690±10	22±2	1

3 RESULTS AND DISCUSSION

3.1 Characterization of Activated Carbon

Results of the physical characteristics of activated carbons are given in Table 2. Bulk density of groundnut husk activated carbon is lower as compared with groundnut foliage and Groundnut (Arachis hypogaea) because of its powdered nature. Percentage loss on ignition is higher for groundnut foliage activated carbon indicating its high carbon content. Surface area is very high in case of groundnut husk activated carbon due to its smaller particle size, which shows the possibility of high adsorptive nature. However compared to GFAC and LAAC, GHAC is less adsorption capacity.

Table 2: Bulk density of Activated Carbon

S.NO	TYPES OF ACTIVATED CARBON	BULK DENSITY (mg/cc)
1	GFAC	0.259
2	GHAC	0.5

Note: GNFAC – Groundnut foliage Activated Carbon & GNHAC - Groundnut husk Activated Carbon

3.2 SEM

The surface morphology of activated carbon is prepared using the groundnut foliage and husks are depicted in figures (2, 3, 4 & 5). SEM images of adsorbents were taken to know the pores and cavities for effective adsorption for the adsorbent. The more pores and cavities clearly showed the good possibility of Cr (VI) content to be trapped and adsorbed into these pores in groundnut foliage than the groundnut husk.
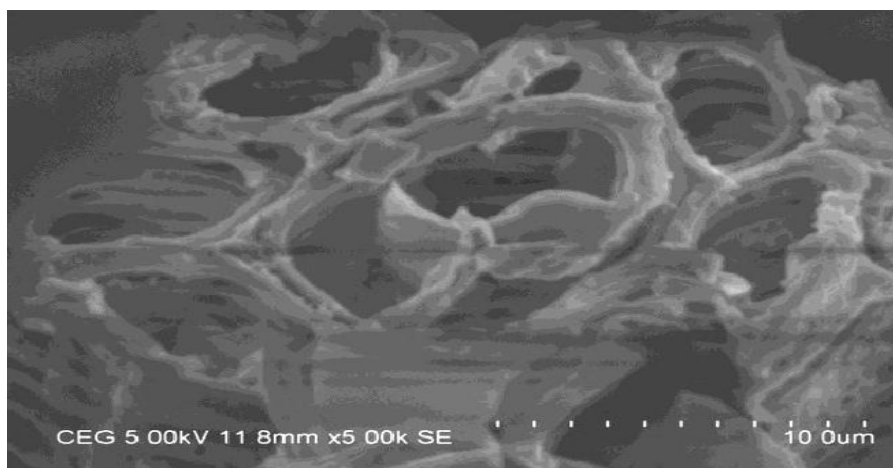
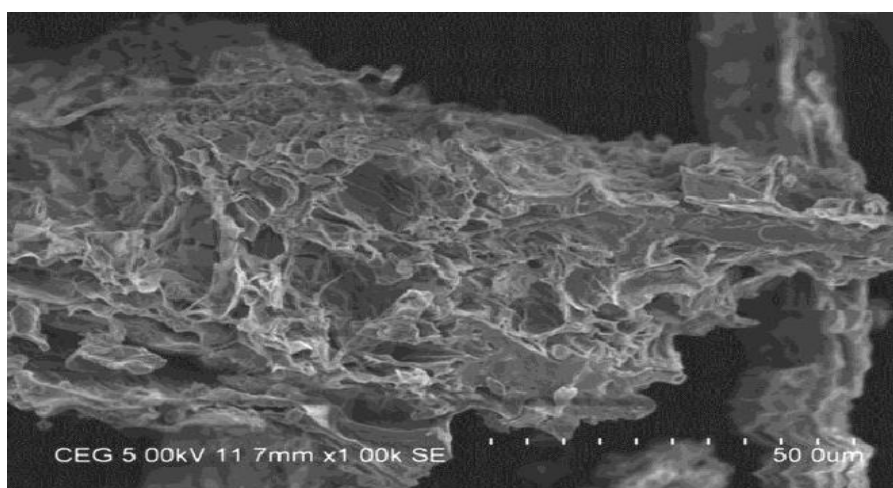**Figure 2: GFAC SEM analysis of adsorbent before adsorption**

Figure 3: GFAC Carbon SEM analysis of adsorbent after adsorption

Figure 4: GHAC SEM analysis of adsorbent before adsorption

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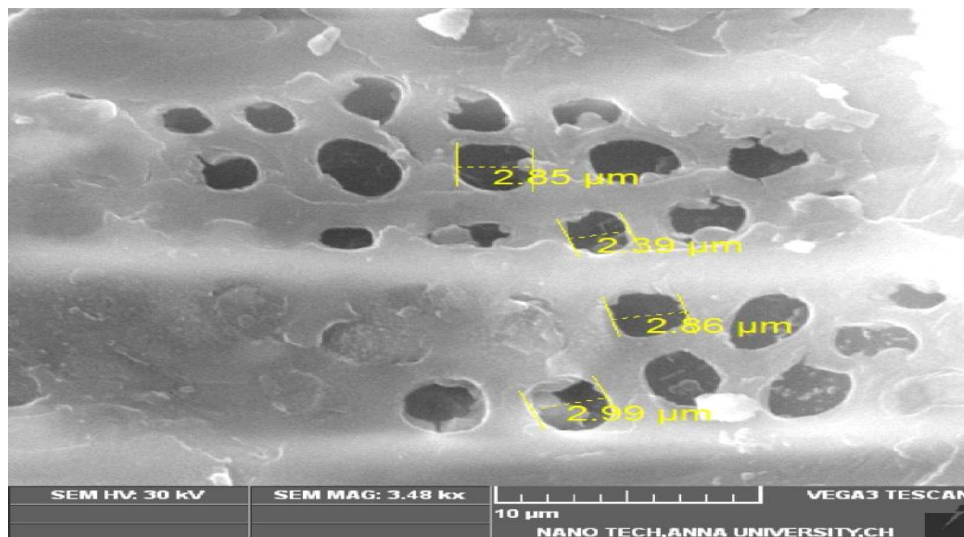*Eur. Chem. Bull. 2023,12(12), 1680-1698*

Figure 5: GHAC SEM analysis of adsorbent after adsorption

3.3 FTIR

The FTIR spectroscopy analysis of groundnut husk activated carbon was made in the range of 4800 to 415 cm^{-1} region.
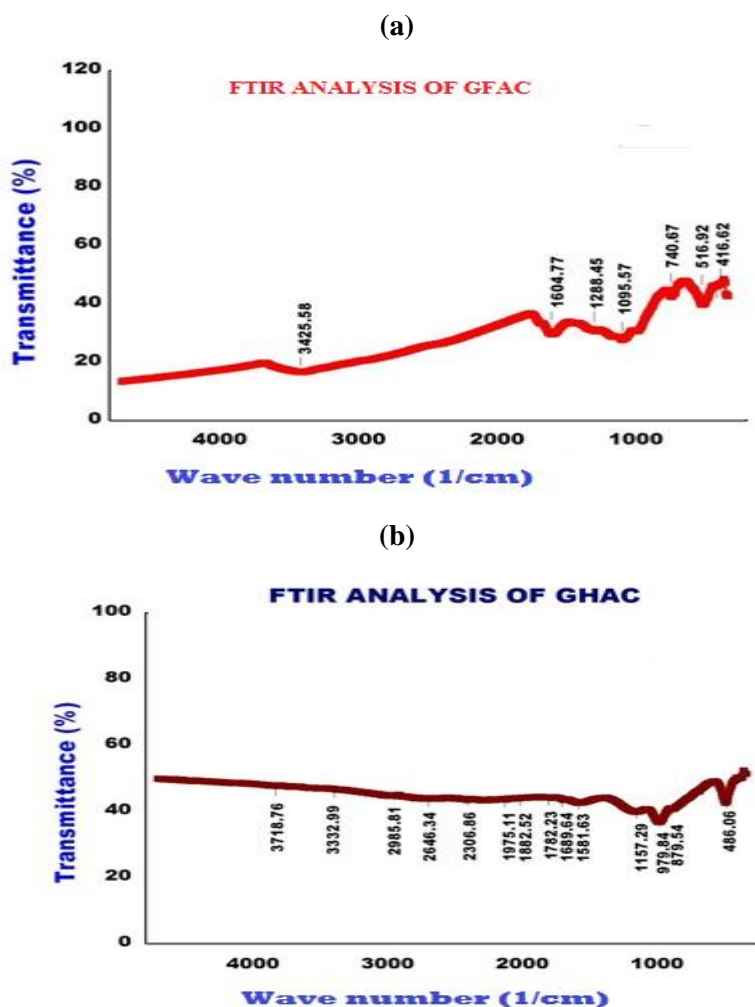
(a)

(b)

Figure 6: FTIR Analyses of (a) GFAC and (b) GHAC

The functional groups which represent surface functionality of the groundnut foliage and groundnut husk activated carbons were listed in table the following table (3&4).

Table 3: FTIR Analysis of Groundnut Foliage

S.NO	Wave number (cm^{-1})	Functional Group	Intensity
1	3989	-OH	Medium
2	3425	-OH	Medium
3	1604	-C=O	Strong
4	1288	-COOH	Medium
5	1095	Ether C-O	Strong
6	740	PO$_4$	Strong and Sharp
7	416	N-containing bio-ligand	Strong and Sharp

Table 4: FTIR Analysis of Groundnut Husk

S.NO	Wave number (cm^{-1})	Functional Group	Intensity
1	3718	-OH	Medium
2	3332	-OH	Medium
3	2985	Alkaline C-H	Medium
4	1689	-C=O	Strong
5	1581	-COOH	Medium
5	1157	Ether C-O	Strong
6	979	PO$_4$	Strong and Sharp
7	486	N-containing bio-ligand	Strong and Sharp

XRD Analyses of Activated carbon GFAC and GHAC

Figure 7 (a, b) shows the XRD pattern of the lotus leaf adsorbent. The diffraction at 2θ 29 and 40° is related to Calcium Carbonate and the diffraction at 2θ 28 and 34° is related to Potassium Chloride. According to Debye-Scherrer equation, the average crystallite size of Lotus leaf adsorbent crystals were determined 25.12 nm.
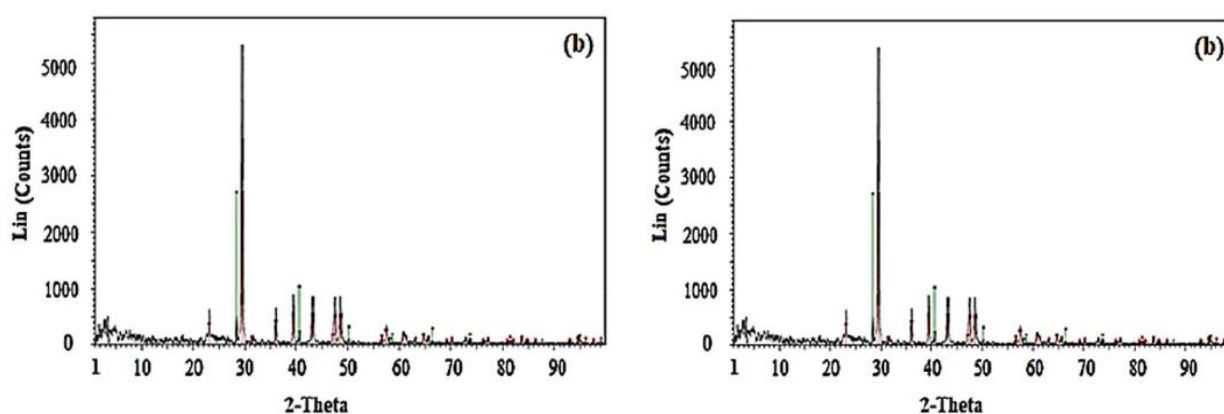
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Figure 7: XRD pattern of (a) GFAC and (b) GHAC

Also, the spectra in 2θ 0.499 and 0.998 are related to empty cavities in the adsorbent. Also, in the XRD analysis after adsorption, spectra in 2θ 29 and 40° are related to Calcium Carbonate and the spectra in 2θ 28 and 34° are related to Potassium Chloride. According to Debye-Scherrer equation, the average crystallite size of Lotus leaf adsorbent was determined 29.88 nm. By comparing the graphs before and after adsorption, it can be seen that both graphs have very similar peaks which shows that the adsorbent structure has not changed much after adsorption.

3.4 Effect of pH

The pH of groundwater is a significant factor for the adsorption of Cr (VI) on both the activated carbons, which shows the effect of pH on adsorption.
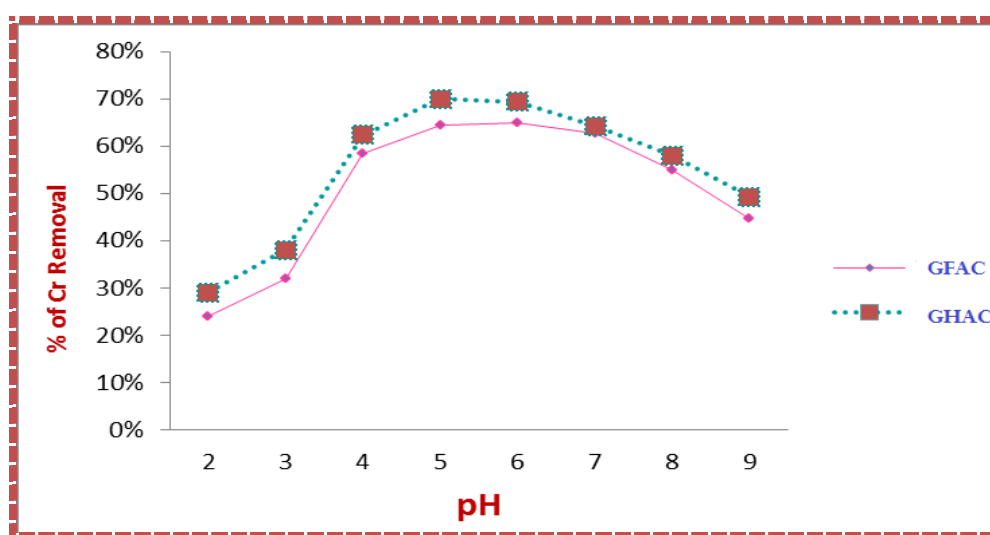

Figure 8: Effect of pH on Cr (VI) content removal

The extreme Cr (VI) removal was detected at pH of 6 for both the activated carbons after this pH level, the removal percentage is decreased from 69% to 66% and 58% to 55% on activated carbon of groundnut foliage and groundnut husk respectively. The maximum adsorption was observed for Cr (VI) content at pH 4 in activated carbon of Groundnut (Arachis hypogaea).

3.5 Effect of Contact Time

The effect of contact time on the removal of Cr (VI) content is shown in fig. 9 80% and 68% Cr (VI) content removal takes place in 240 min for activated carbon of groundnut foliage and groundnut husk respectively. However the Groundnut (Arachis hypogaea) takes place in 60 min to remove only 11.4% of Cr (VI) content. The equilibrium was reached after 240min. The change in the rate of adsorption could be due to fact that initially all the adsorbent sites are vacant and solute concentration gradient is very high. Later, the lower adsorption rate is due to a decrease in number of empty sites of adsorbent & Cr (VI) content concentrations. Adsorption rate decreases showed particularly, termination of the trials. This can be attributed to the absence of available active site mandatory for the further uptake after achieving the

equilibrium. From the data, groundnut foliage of activated carbon gives the better result than the groundnut husk.
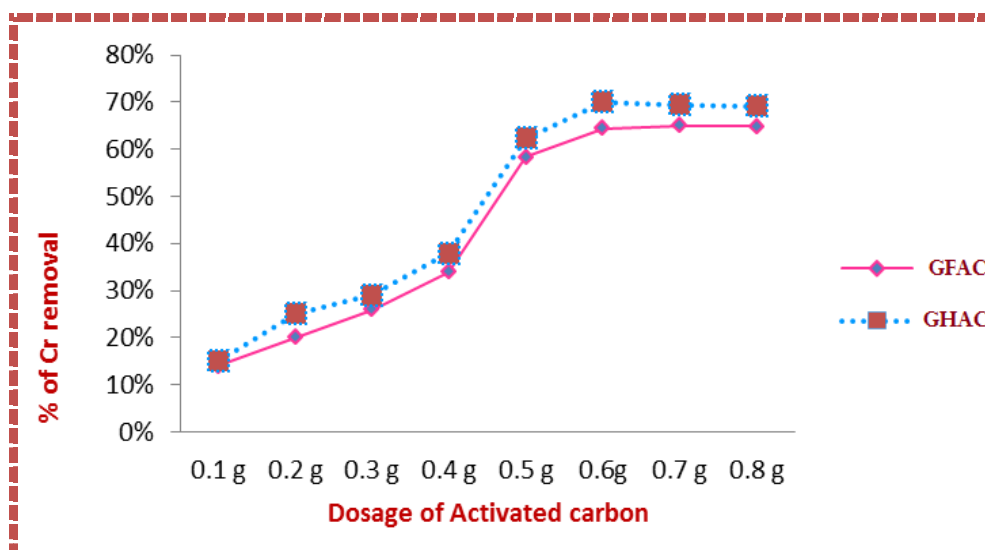

Figure 9: Effect of time on Cr (VI) content removal

3.6 Effect of Adsorbent Dosage

The effect of carbon dose on the uptake of Cr (VI) content a sequence of adsorption experimentations were approved out with different dosages varying from 0.1 g to 0.7g/50 ml at the concentration of 150 ppm. The carbon dosage for the adsorption of Cr (VI) content through groundnut foliage and husk of activated carbon was started to increase (39% to 93% and 36% to 78% respectively) by increasing the adsorbent dose, owing to the rise of the activated site open for the adsorption. The removal percentage increased sharply with an increase in the adsorbent concentration from 0.1g to 0.5g/100 ml. However, no drastic changes in removal efficiency were observed beyond 0.5g/100 ml adsorbent dosage. If 0.5g/100ml is considered, the optimal dose for other loadings. If 9g of Activated carbon of Groundnut (Arachis hypogaea) was removed only 25% of Cr (VI) content.
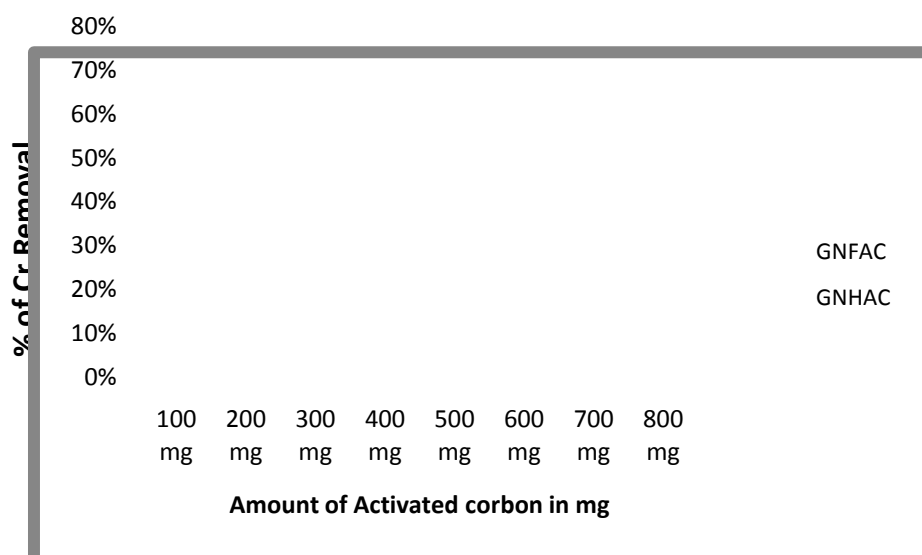

Figure 10: Effect of adsorbent dosage on Cr (VI) content

6.3.7 Adsorption Isotherm Modeling

Adsorption Isotherm Studies

In this study, two important isotherm models, the Freundlich and Langmuir models were examined to identify the best fit model. The adsorption isotherm is helpful for representing the relationship between the equilibrium amounts of Cr (VI) on the adsorbent surface and plays a vital role in identifying the adsorption limit. The Freundlich model assumes that adsorption takes place on heterogeneous sites of the adsorbent material and has a multi-layered uptake, whereas the Langmuir isotherm assumes that adsorption takes place on homogeneous sites. A graph plot between 'lnC_e' vs. 'lnQ_e'(Figure6a) corresponded to a straight line with an intercept lnK and slope (1/n) in the Freundlich model, and '$1/Q_e$' vs. '$1/C_e$' corresponded to a straight line in the Langmuir model(Figure 6b) using GNFAC & GNHAC with same tannery waste water samples.

Freundlich's isotherm and Langmuir isotherm for adsorption of Cr (VI) content onto optimized activated carbon of groundnut foliage and groundnut husk are shown in fig 6.7. The isotherm signifies the specific relation among the concentration of Adsorbate and its degrees to addition on adsorbent surface.(Table 6.4) It has exposed that, the values of coefficient in Freundlich's isotherm (R^2 = 0.9913 and R^2 = 0.991) was higher than the Langmuir isotherm (R^2 = 0.9672 and R^2 = 0.9767) on groundnut foliage and husk of activated carbon respectively. Fig 6.7 showed that, the isotherm data better fitted in the Freundlich's equation than Langmuir equation[10]. The experimental data for adsorption of Cr (VI) content on activated carbon have been fitted both Langumuir and Freundlich's model. But small values of correlation co-efficient showed that Langumuir model is less fitted current adsorption compared with Freundlich's model for both the activated carbon. In common, according to R^2 standard, Freundlich's model fits improved for Cr (VI) content adsorption for existing adsorption study.

Table 5: Freundlich and Langmuir adsorption isotherm equation

Adsorption Models	Linear Forms	Graph Drawn between
Freundlich Model	$lnQ_e = lnK_f + \frac{1}{n_f}lnC_e$	lnC_e versus lnQ_e
Langmuir Model	$\frac{1}{Q_e} = \frac{1}{Q_m bC_e} + \frac{1}{Q_m}$	$1/C_e$ versus $1/Q_e$

Table 6: Langmuir and Freundlich's constant for Cr (VI) content adsorption

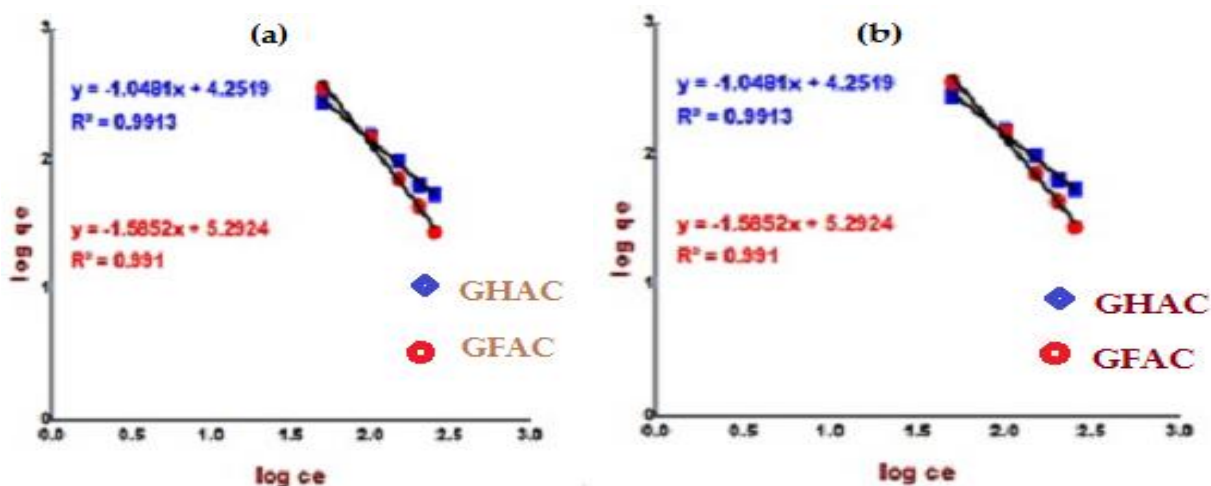| Activated Carbon	Langmuir Constant		Freundlich's Constant	
	K (mg/g)	R^2	lnK_F	R^2
Groundnut Foliage	50	0.9672	4.2	0.9913
Groundnut Husk	0.07	0.9767	5.2	0.991

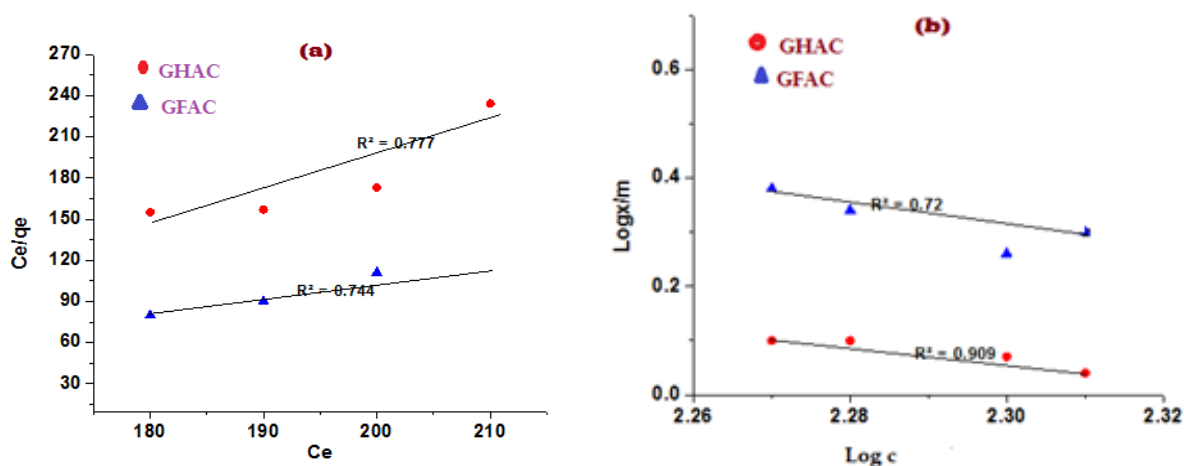**Figure 11: (a) Langmuir and (b) Freundlich's isotherms for GNHAC & GNFAC**

Figure 12: (a) Langmuir and (b) Freundlich's isotherms for GHAC & GFAC

Table 7: Pseudo-first orders and Pseudo-second order kinetic equations

Adsorption Kinetic Models	Linear Forms	Graph Drawn between
Pseudo-first-order	$ln(Q_e - Q_t) = lnQ_e - K_1t$	t verses $ln(Q_e - Q_t)$
Pseudo-second-order	$\frac{t}{Q_t} = \frac{1}{K_2Q_e^2} + \frac{1}{Q_e}t$	t verses $\frac{t}{Q_t}$

Table 8: The data of Pseudo-first orders and Pseudo-second order kinetic model constant for the adsorption of l Cr (VI) adsorption on GFAC

Adsorbate (GF)(mg/l)	Pseudo-first order kinetic			Pseudo-second order kinetic		
	K_1 (min)$^{-1}$	q_e (mg/g)	R^2	K_2 (min)$^{-1}$	q_e (mg/g)	R^2
100	0.036	1.87	0.893	112.3	0.0089	0.995
200	0.028	2.16	0.899	105.26	0.0095	0.991
300	0.026	2.31	0.896	113.6	0.0088	0.992
400	0.023	2.40	0.909	95.23	0.0105	0.963
500	0.033	2.54	0.920	113.6	0.0088	0.960

The regression coefficient of above 0.99 is considered to be important factor and from figure 6.8 and 6.9 respective coefficients were calculated and found the adsorption follows pseudo-Second-order kinetic model which confirms the chemisorption's of hexavalent chromium content on both the activated carbon of groundnut foliage and husk.

Table 8: The data of Pseudo-first orders and Pseudo-second order kinetic model constant for the adsorption of l Cr (VI) adsorption on GHAC

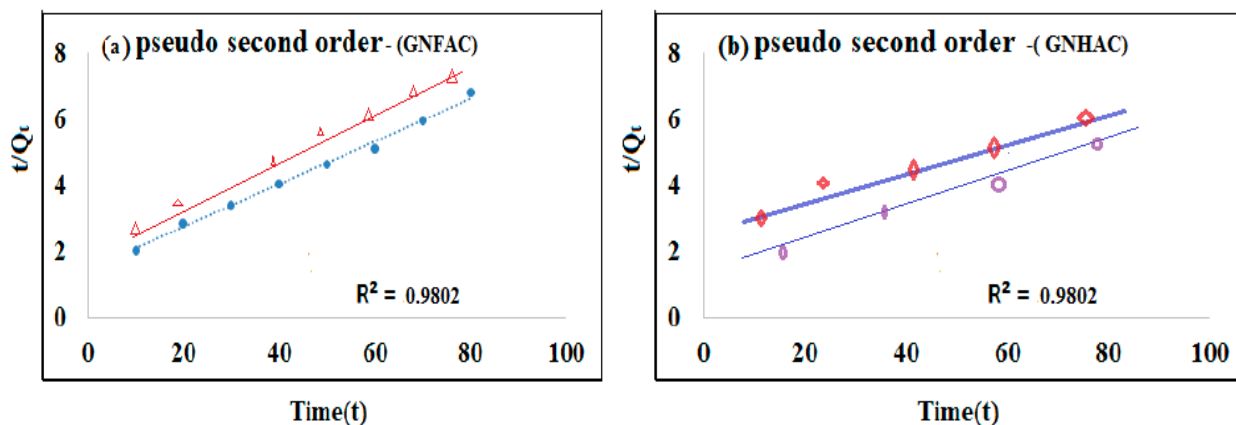| Adsorbate (GF) (mg/l)	Pseudo-first order kinetic			Pseudo-second order kinetic		
	K_1 (min)$^{-1}$	q_e (mg/g)	R^2	K_2 (min)$^{-1}$	q_e (mg/g)	R^2
100	0.032	1.88	0.873	119.87	0.0091	0.991
200	0.029	2.18	0.919	101.67	0.0098	0.934
300	0.025	2.38	0.898	117.42	0.0086	0.997
400	0.021	2.42	0.919	96.87	0.0108	0.973
500	0.037	2.58	0.928	119.2	0.0085	0.971

Fig 13: Pseudo-first orders and Pseudo-second order kinetic model constant for the adsorption of l Cr (VI) adsorption on GNFAC & GNHAC

Regeneration study on Cr (VI) ion adsorption

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Desorption study of exhausted carbon and recovery of Cr (VI) ions contribute to the economy of waste water treatment. Desorption of Cr (VI) ions by KOH.HSO$_4$, and distilled water are presented as bar diagram in Figure 14. Sodium hydroxide is a better reagent for desorption of Cr (VI) ions, because 69% of adsorbed Cr (VI) ions were removed from GHAC & GFAC. Degeneracy of Cr (VI) ion by GHAC somewhat greater than GFAC .

Regeneration of adsorbent

The adsorption method is economical if the adsorbent is reused. Reuse of GFAC & GHAC from Cr (VI)-loaded material is studied for sorption and desorption cycles using sodium hydroxide as a regenerating agent. Four different desorption agents, such as tap water 0.1 M H$_2$SO4 and 0.1 M KOH are used to remove the adsorbed chromium ions from the GFAC & GHAC adsorbent. Cr (VI) desorption studies were performed using 10 g of Cr (VI)-loaded adsorbent with 100mL desorption agents in 250 mL conical flasks under a desorption agent. After reusing of regenerated adsorbent for Cr (VI) removal, the loaded adsorbent was again regenerated by the same procedure demonstrated previously for consecutive cycles. Numerous regenerations and the following use for the removal Cr (VI) are completed and the obtained results are shown in Figure 14. It is decided the graph that there is a reduction in the percentage removal of Cr (VI) with an increase the regeneration cycle, the removal percentage was still above 70%. Therefore, GHAC & GFAC has a more re-usage potential for the Cr (VI) [54-60].
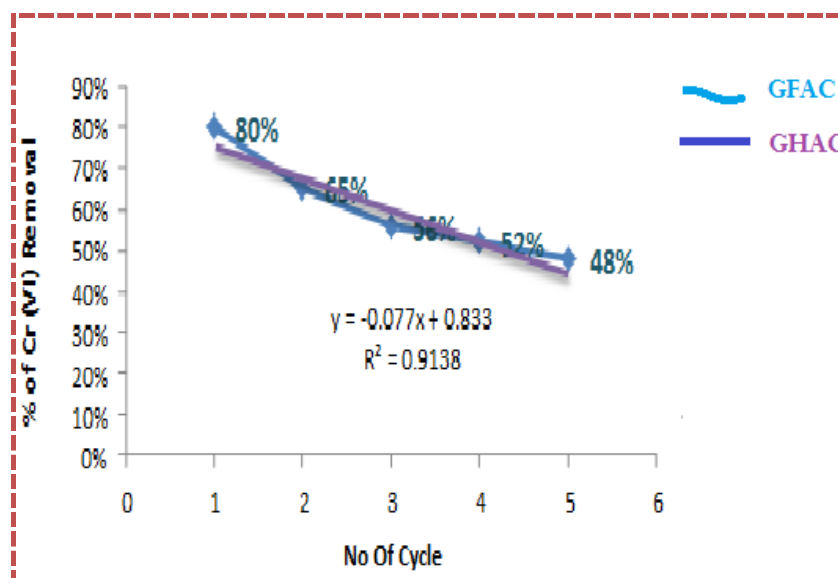

Fig 14: % Removal of Cr (VI) from the prepared (GFAC & GHAC) adsorbent and regenerated adsorbent of several cycles.

Cost Estimation

Economic viability is a prerequisite for the decontamination of water in tannery industrial areas – Ranipet Taluk. Tannery waste water is widely available as a bio-waste. Cost estimation was performed for the prepared adsorbent (GFAC & GHAC), which offers a good option for Cr (VI) adsorption. The groundnut plants were collected from local cultivation land at free of cost. The cost of the drying process and chemicals utilized led to an approximate cost of 700 to 800 INR per kilogram of prepared adsorbent, which was lower than that of the commercially available activated carbon generally utilized in the Cr (VI) removal treatment.

4. CONCLUSIONS

In this work activated carbon prepared from groundnut foliage and   husk as a potential adsorbent for the removal of Cr (VI) ions from the tannery waste water. They prepared by chemical activation method with different activating conditions (Activating agent- KOH, ZnCl2 and H_3PO_4; Impregnation ratio-1:1, 1:2, 1:2; Activation temeperture-500-700°C). Experimental results and predicted values were well fitted in the quadratic model. The GFAC and GHAC activated carbon prepared based on optimized condition has well-developed pore structure and functional groups which is confirmed from SEM images, XRD and FTIR analyses respectively. The adsorption equilibrium was reached in 240 minutes with the isotherm data fitted well in Langmuir model and Freundlich's model indicating a chemisorptions adsorption for the activated carbon. Equilibrium with the data with R2 higher than Langmuir isotherm data confirms that the system follows Freundlich's model. The data indicate that the adsorption kinetics follow the pseudo-second-order rate. From the results it is very much evident that the prepared AC (GFAC and GHAC) possess the ability the organic removal from water.   Desorption studies were also carried out using various reagents. NaOH was found to be most effective reagent for the displacement of Cr (VI) ions. This result also favored the physisorption mechanism.

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CONFLICTS OF INTEREST:

The authors have no conflict of interest to declare that are relevant to the content of this article.

REFERENCES

1. Liang, Sha, Xueyi Guo, Silke Lautner, and Bodo Saake. "Removal of hexavalent chromium by different modified spruce bark adsorbents." Journal of Wood Chemistry and Technology 34, no. 4 (2014): 273-290.
2. Padavathy, K. S., G. Madhu, and P. V. Haseena. "A study on effects of pH, adsorbent dosage, time, initial concentration and adsorption isotherm study for the removal of hexavalent chromium (Cr (VI)) from wastewater by magnetite nanoparticles." Procedia Technology 24 (2016): 585-594.
3. Aranda-García, Erick, and Eliseo Cristiani-Urbina. "Effect of pH on hexavalent and total chromium removal from aqueous solutions by avocado shell using batch and continuous systems." Environmental Science and Pollution Research 26, no. 4 (2019): 3157-3173.
4. Ali, Ashraf, Khalid Saeed, and Fazal Mabood. "Removal of chromium (VI) from aqueous medium using chemically modified banana peels as efficient low-cost adsorbent." Alexandria Engineering Journal 55, no. 3 (2016): 2933-2942.

5. A Kistan, A., A. Premkumar & V. Kanchana, A Simple Treatment of Tannery Wastewater using Modified Activated Carbon by Metal Chloride, Asian J. Chem. / 2022 / 34(7) / pp 1698-1702 https://doi.org/10.14233/ajchem.2022.23699

6. Choudhary, Bharat, and Debajyoti Paul. "Isotherms, kinetics and thermodynamics of hexavalent chromium removal using biochar." Journal of Environmental Chemical Engineering 6, no. 2 (2018): 2335-2343.

7. Narayanasamy, Saranya, Vickram Sundaram, Thanigaivel Sundaram, and Dai-Viet N. Vo. "Biosorptive ascendency of plant based biosorbents in removing hexavalent chromium from aqueous solutions–Insights into isotherm and kinetic studies." Environmental Research 210 (2022): 112902.

8. Wassie, Abrham Bayeh, and Vimal Chandra Srivastava. "Teff straw characterization and utilization for chromium removal from wastewater: Kinetics, isotherm and thermodynamic modelling." Journal of Environmental Chemical Engineering 4, no. 1 (2016): 1117-1125.

9. Shooto, Ntaote David. "Removal of toxic hexavalent chromium (Cr (VI)) and divalent lead (Pb (II)) ions from aqueous solution by modified rhizomes of Acorus calamus." Surfaces and Interfaces 20 (2020): 100624.

10. Ntuli, Themba Dominic, and Vusumzi Emmanuel Pakade. "Hexavalent chromium removal by polyacrylic acid-grafted Macadamia nutshell powder through adsorption–reduction mechanism: adsorption isotherms, kinetics and thermodynamics." Chemical Engineering Communications 207, no. 3 (2020): 279-294.

11. Kistan, A., & V. Kanchana, Confiscation of chemical oxygen demand from groundwater samples collected from near tanneries using activated carbon of Ricinus Communis blended with coconut shell. Indian Journal of Environmental Protection Volume 40, Issue 5, Pages 527 – 532, 2020.

12. A Kistan, Andiyappan, V. Kanchana, Silver-Alumina Impregnated Maghemite/Magnetite Nanocomposites for Effective Removal of Chromium(VI) from the Tannery Discharge, Asian J. Chem. / 2023 / 35(8) / pp 1899-1906., https://doi.org/10.14233/ajchem.2023.27792

13. Ntuli, T. D., T. H. Mongwe, L. L. Sikeyi, O. Mkhari, N. J. Coville, E. N. Nxumalo, and M. S. Maubane-Nkadimeng. "Removal of hexavalent chromium via an adsorption coupled reduction mechanism using olive oil derived carbon nano-onions." Environmental Nanotechnology, Monitoring & Management 16 (2021): 100477.

14. Rai, M. K., Garima Shahi, V. Meena, Roshni Meena, S. Chakraborty, R. S. Singh, and B. N. Rai. "Removal of hexavalent chromium Cr (VI) using activated carbon prepared from mango kernel activated with H3PO4." Resource-efficient technologies 2 (2016): 63-70.

15. Sharma, Pushpendra Kumar, Sohail Ayub, and Chandra Nath Tripathi. "Isotherms describing physical adsorption of Cr (VI) from aqueous solution using various agricultural wastes as adsorbents." Cogent Engineering 3, no. 1 (2016): 1186857.

16. Khan, Taimur, Mohamed Hasnain Isa, Muhammad Raza Ul Mustafa, Ho Yeek-Chia, Lavania Baloo, Teh Sabariah Binti Abd Manan, and Mohamed Osman Saeed. "Cr (VI) adsorption from aqueous solution by an agricultural waste based carbon." RSC advances 6, no. 61 (2016): 56365-56374.

17. Sultana, Marzia, Mahbub Hasan Rownok, Meherunnesa Sabrin, Md Hafezur Rahaman, and SM Nur Alam. "A review on experimental chemically modified activated carbon to enhance dye and heavy metals adsorption." Cleaner Engineering and Technology 6 (2022): 100382.

18. Chakraborty, Rupa, Anupama Asthana, Ajaya Kumar Singh, Renu Verma, Sreevidya Sankarasubramanian, Sushma Yadav, Sónia AC Carabineiro, and Md Abu Bin Hasan Susan. "Chicken feathers derived materials for the removal of chromium from aqueous solutions: kinetics, isotherms, thermodynamics and regeneration studies." Journal of Dispersion Science and Technology 43, no. 3 (2022): 446-460.

19. Kebede, Abayneh, Kassim Kedir, Fekadu Melak, and Tsegaye Girma Asere. "Removal of Cr (VI) from aqueous solutions using biowastes: tella residue and pea (Pisum sativum) seed shell." The Scientific World Journal 2022 (2022).

20. Kistan, A., V. Kanchana, L. Sakayasheela, J. Sumathi, A. Premkumar, and A. Selvam. "Titanium dioxide as a Catalyst for Photodegradation of Various Concentrations of Methyl Orange and Methyl Red dyes using Hg Vapour Lamp with Constant pH." Oriental Journal of Chemistry 34, no. 2 (2018). http://dx.doi.org/10.13005/ojc/340250

21. Mahmoud, Mohamed E., Asmaa K. Mohamed, and Mohamed Abdel Salam. "Self-decoration of N-doped graphene oxide 3-D hydrogel onto magnetic shrimp shell biochar for enhanced removal of hexavalent chromium." Journal of Hazardous Materials 408 (2021): 124951.

22. Altun, Turkan, Şerife Parlayıcı, and Erol Pehlivan. "Hexavalent chromium removal using agricultural waste "rye husk"." Desalination and Water Treatment 57, no. 38 (2016): 17748-17756.

23. Islam, Izaz Ul, Mushtaq Ahmad, Maqbool Ahmad, Shah Rukh, and Ihsan Ullah. "Kinetic studies and adsorptive removal of chromium Cr (VI) from contaminated water using green adsorbent prepared from agricultural waste, rice straw." European Journal of Chemistry 13, no. 1 (2022): 78-90.

24. Nasseh, N., L. Taghavi, B. Barikbin, and M. Khodadadi. "Advantage of almond green hull over its resultant ash for chromium (VI) removal from aqueous solutions." International Journal of Environmental Science and Technology 14, no. 2 (2017): 251-262.

25. Borna, Mohammad Omidvar, Meghdad Pirsaheb, Mehdi Vosoughi Niri, Reza Khosravi Mashizie, Babak Kakavandi, Mohammad Reza Zare, and Anvar Asadi. "Batch and column studies for the adsorption of chromium (VI) on low-cost Hibiscus Cannabinus kenaf, a green adsorbent." Journal of the Taiwan Institute of Chemical Engineers 68 (2016): 80-89.

26. Hussain, Athar, Sangeeta Madan, and Richa Madan. "Removal of heavy metals from wastewater by adsorption." Heavy Metals—Their Environmental Impacts and Mitigation (2021).

27. Ayele, Abate, and Yakob Godebo Godeto. "Bioremediation of chromium by microorganisms and its mechanisms related to functional groups." Journal of Chemistry 2021 (2021).

28. Giri, Deen Dayal, Maulin Shah, Neha Srivastava, Abeer Hashem, Elsayed Fathi Abd_Allah, and Dan Bahadur Pal. "Sustainable chromium recovery from wastewater using mango and jackfruit seed kernel bio-adsorbents." Frontiers in Microbiology 12 (2021): 717848.

29. Gaikwad, Mahendra S., and Chandrajit Balomajumder. "Simultaneous rejection of chromium (VI) and fluoride [Cr (VI) and F] by nanofiltration: Membranes characterizations and estimations of membrane

transport parameters by CFSK model." Journal of environmental chemical engineering 5, no. 1 (2017): 45-53.

30. Qureshi, Muhammad I., Faheemuddin Patel, Nadhir Al-Baghli, Basim Abussaud, Bassam S. Tawabini, and Tahar Laoui. "A comparative study of raw and metal oxide impregnated carbon nanotubes for the adsorption of hexavalent chromium from aqueous solution." Bioinorganic chemistry and applications 2017 (2017).

31. Alalwan, Hayder A., Mohammed A. Kadhom, and Alaa H. Alminshid. "Removal of heavy metals from wastewater using agricultural byproducts." Journal of Water Supply: Research and Technology-Aqua 69, no. 2 (2020): 99-112.

32. Ibrahim, Bnar Mahmoud. "Heavy metal ions removal from wastewater using various low-cost agricultural wastes as adsorbents: a survey." Zanco Journal of Pure and Applied Sciences 33, no. 2 (2021): 76-91.

33. Prabhu, Prathiksha P., and Balakrishna Prabhu. "A review on removal of heavy metal ions from waste water using natural/modified bentonite." In MATEC Web of conferences, vol. 144, p. 02021. EDP Sciences, 2018.

34. Nag, Soma, Abhijit Mondal, Nirjhar Bar, and Sudip Kumar Das. "Biosorption of chromium (VI) from aqueous solutions and ANN modelling." Environmental Science and Pollution Research 24, no. 23 (2017): 18817-18835.

35. Sheth, Yashvi, Swapnil Dharaskar, Mohammad Khalid, and Shriram Sonawane. "An environment friendly approach for heavy metal removal from industrial wastewater using chitosan based biosorbent: A review." Sustainable Energy Technologies and Assessments 43 (2021): 100951.

36. Tamjidi, Sajad, Hossein Esmaeili, and Bahareh Kamyab Moghadas. "Application of magnetic adsorbents for removal of heavy metals from wastewater: a review study." Materials Research Express 6, no. 10 (2019): 102004.

37. Alagarsamy, Vijaya Anandan Veerasamy, **Kistan Andiyappan**, Saral Abdul Kadar Avuliya, and Thaminum Ansari Abubacker. "Retarding of Preliminary Chemical Pollutants from Dye Effluent by Metal Nano Particles Synthesized using Flower Extract of Catharanthus Roseus." Oriental Journal of Chemistry 34, no. 1 (2018): 381. http://dx.doi.org/10.13005/ojc/340141

38. Song, Dagang, Kaiwen Pan, Akash Tariq, Azizullah Azizullah, Feng Sun, Zilong Li, and Qinli Xiong. "Adsorptive removal of toxic chromium from waste-water using wheat straw and Eupatorium adenophorum." PloS one 11, no. 12 (2016): e0167037.

39. Joseph, Lesley, Byung-Moon Jun, Joseph RV Flora, Chang Min Park, and Yeomin Yoon. "Removal of heavy metals from water sources in the developing world using low-cost materials: A review." Chemosphere 229 (2019): 142-159.

40. Rasheed, Tahir, Adeel Ahmad Hassan, Muhamad Bilal, Tariq Hussain, and Komal Rizwan. "Metal-organic frameworks based adsorbents: A review from removal perspective of various environmental contaminants from wastewater." Chemosphere 259 (2020): 127369.

41. Qasem, Naef AA, Ramy H. Mohammed, and Dahiru U. Lawal. "Removal of heavy metal ions from wastewater: A comprehensive and critical review." Npj Clean Water 4, no. 1 (2021): 1-15.

42. Yadav, Sarita, Aruna Yadav, Nisha Bagotia, Ashok K. Sharma, and Surender Kumar. "Adsorptive potential of modified plant-based adsorbents for sequestration of dyes and heavy metals from wastewater-A review." Journal of Water Process Engineering 42 (2021): 102148.

43. Gupta, G., J. Khan, and N. K. Singh. "Application and efficacy of low-cost adsorbents for metal removal from contaminated water: A review." Materials Today: Proceedings 43 (2021): 2958-2964.

44. Chakraborty, Rupa, Anupama Asthana, Ajaya Kumar Singh, Bhawana Jain, and Abu Bin Hasan Susan. "Adsorption of heavy metal ions by various low-cost adsorbents: a review." International Journal of Environmental Analytical Chemistry 102, no. 2 (2022): 342-379.

45. Anderson, A., A. Anbarasu, Raghavendra Rao Pasupuleti, M. Sekar, T. R. Praveenkumar, and J. Aravind Kumar. "Treatment of heavy metals containing wastewater using biodegradable adsorbents: A review of mechanism and future trends." Chemosphere (2022): 133724.

46. Tamjidi, Sajad, Bahareh Kamyab Moghadas, Hossein Esmaeili, Farideh Shakerian Khoo, Gholamhossein Gholami, and Mansoure Ghasemi. "Improving the surface properties of adsorbents by surfactants and their role in the removal of toxic metals from wastewater: A review study." Process Safety and Environmental Protection 148 (2021): 775-795.

47. Gu, Shiqing, Xiaonan Kang, Lan Wang, Eric Lichtfouse, and Chuanyi Wang. "Clay mineral adsorbents for heavy metal removal from wastewater: a review." Environmental Chemistry Letters 17, no. 2 (2019): 629-654.

48. Kaur, Simran, and Arpita Roy. "Bioremediation of heavy metals from wastewater using nanomaterials." Environment, Development and Sustainability 23, no. 7 (2021): 9617-9640.

49. Fouda-Mbanga, B. G., E. Prabakaran, and K. Pillay. "Carbohydrate biopolymers, lignin based adsorbents for removal of heavy metals (Cd2+, Pb2+, Zn2+) from wastewater, regeneration and reuse for spent adsorbents including latent fingerprint detection: A review." Biotechnology Reports 30 (2021): e00609.

50. Fei, Yuhuan, and Yun Hang Hu. "Design, synthesis, and performance of adsorbents for heavy metal removal from wastewater: a review." Journal of Materials Chemistry A (2022).

51. Ugwu, E. I., O. Tursunov, D. Kodirov, L. M. Shaker, A. A. Al-Amiery, I. Yangibaeva, and F. Shavkarov. "Adsorption mechanisms for heavy metal removal using low cost adsorbents: A review." In IOP Conference Series: Earth and Environmental Science, vol. 614, no. 1, p. 012166. IOP Publishing, 2020.

52. Ogata, Fumihiko, Noriaki Nagai, Ryo Itami, Takehiro Nakamura, and Naohito Kawasaki. "Potential of virgin and calcined wheat bran biomass for the removal of chromium (VI) ion from a synthetic aqueous solution." Journal of Environmental Chemical Engineering 8, no. 2 (2020): 103710.

53. Golestanifar, H. A. F. E. Z., Behzad Haibati, Hassan Amini, MOHAMMAD HADI Dehghani, and Anvar Asadi. "Removal of hexavalent chromium from aqueous solution by adsorption on γ-alumina nanoparticles." Environment protection engineering 41, no. 2 (2015): 133-145.

54. Altun, Türkan, Hüseyin Ecevit, Yakup Kar, and Birsen Çiftçi. "Adsorption of Cr (VI) onto cross-linked chitosan-almond shell biochars: equilibrium, kinetic, and thermodynamic studies." Journal of Analytical Science and Technology 12, no. 1 (2021): 1-15.

55. GAO, Huan, Anlei WEI, Xiaoqing ZHENG, and Yixuan ZHANG. "Adsorption of hexavalent chromium from aqueous solution by acetylated wheat straw." Chinese Journal of Environmental Engineering 10, no. 9 (2016): 4753-4760.

56. Bhusari, V. N., Rashmi Dahake, Sadhana Rayalu, and Amit Bansiwal. "Comparative study of removal of hexavalent chromium from water using metal oxide nanoparticles." Advances in Nanoparticles 5, no. 1 (2016): 67-74.

57. Huang, Haihong, Deliang He, Yining Tang, Yanni Guo, Ping Li, Wei Qv, Fan Deng, and Fuhui Lu. "Adsorption of hexavalent chromium from an aqueous phase by hydroxypropyl methylcellulose modified with diethylenetriamine." Journal of Chemical & Engineering Data 64, no. 1 (2018): 98-106.

58. Li, Jingyi, Jie Ma, Qiehui Guo, Shenglong Zhang, Huayun Han, Shusheng Zhang, and Runping Han. "Adsorption of hexavalent chromium using modified walnut shell from solution." Water Science and Technology 81, no. 4 (2020): 824-833.

59. Bayisa, Yigezu Mekonnen, Tafere Aga Bullo, and Desalegn Abdissa Akuma. "Chromium removal from tannery effluents by adsorption process via activated carbon chat stems (Catha edulis) using response surface methodology." BMC research notes 14, no. 1 (2021): 1-6.

60. Vunain, Ephraim, Joel Brian Njewa, Timothy Tiwonge Biswick, and Adewale Kabir Ipadeola. "Adsorption of chromium ions from tannery effluents onto activated carbon prepared from rice husk and potato peel by H3PO4 activation." Applied Water Science 11, no. 9 (2021): 1-14.

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