PRINT ISSN 1119-8362
Electronic ISSN 2659-1499

Full-text Available Online at
https://www.ajol.info/index.php/jasem
https://www.bioline.org.br/ja

J. Appl. Sci. Environ. Manage.
Vol. 28 (9) 2585-2600 September 2024

Utilization of Base and Acid Modified Rice Husk-Corncobs Composite for Removal of Chromium (VI) Ion in Simulated Tannery Wastewater

***ALHASSAN, AS; OLUBAJO, OO; AHMED, MM**

*[*1]Department of Industrial Chemistry, Faculty of sciences, Mewar International University, Nasarawa, Nigeria*

[2]Department of Chemical Engineering, Faculty of Engineering and Engineering Technology, Abubakar Tafawa Balewa University, Bauchi, Nigeria.

[3]Department of Chemical Engineering, Faculty of Engineering, University of Maiduguri, Borno, Nigeria

**Corresponding Author Email: anassanialhassan@gmail.com, anas.sani@miu.edu.ng*
**ORCID: https://orcid.org/0009-0001-8210-7041*
Tel: +2347034446924

Co-Author Emails: ooolubajo@atbu.edu.ng; mmahmed@unimaid.edu.ng

ABSTRACT: In the ever-increasing blind race of industrialization and urbanization environmental contamination by toxic heavy metal ions is becoming a serious issue for both scientists and masses. Hence, the objective of this paper was to evaluate the utilization of base (BMOD) and acid (AMOD) modified rice husk-corncobs composite for the removal of chromium (VI) Ion in simulated tannery wastewater using appropriate standard techniques. SEM-EDX, XRD and FTIR characterizations revealed the elemental composition, crystallographic structures and the chemical bonds respectively. The results of the sorption kinetic study showed that the data fitted well with the pseudo-second order model for both acid modified (AMOD) and base modified (BMOD) biosorbent with a maximum adsorption of 28.46 mg/g and 39.66 mg/g respectively. The results of the sorption isotherm study showed that they both fitted Freundlich isotherm model. From the results obtained, rice husk and corn cob were effective biosorbent for the removal of Cr (VI) ion from tannery effluent.

DOI: https://dx.doi.org/10.4314/jasem.v28i9.2

Cite this Article as: ALHASSAN, A. S; OLUBAJO, O. O; AHMED, M. M. (2024). Utilization of Base and Acid Modified Rice Husk-Corncobs Composite for Removal of Chromium (VI) Ion in Simulated Tannery Wastewater. *J. Appl. Sci. Environ. Manage.* 28 (9) 2585-2600

Dates: Received: 04 July 2024; Revised: 08 August 2024; Accepted: 12 August July 2024 Published: 05 September 2024

Keywords: rice husk; corncob; biosorbent; wastewater; heavy metal ions

In the ever-increasing blind race of industrialization and urbanization environmental contamination by toxic heavy metals is becoming a serious issue for both scientists and masses. These heavy metal contaminants directly or indirectly affect the health of animals in general and human beings in particular by their incremental accumulation in the soil, plants and water bodies. Effluents of many industries like chemical manufacturing, paper, textile, refinery, petrochemicals, metal manufacturing, electroplating, printing, dye, paint, leather goods manufacturing, fertilizer and pesticides, mining and many more are loaded with various heavy metals and their ions (Sandeep, 2015). Although many different definitions have been proposed to the term "heavy metal," some based on density, some on atomic number or atomic weight, and some on chemical properties, the term is often used to denote a group of metals and semimetals (metalloids) that have been associated with contamination and potential toxicity or ecotoxicity

**Corresponding Author Email: anassanialhassan@gmail.com, anas.sani@miu.edu.ng*
**ORCID: https://orcid.org/0009-0001-8210-7041*
Tel: +2347034446924

(Maria *et al*., 2017). The most commonly occurring metals are Cadmium, Copper, Nickel, Lead, Chromium, Zinc, and Mercury (Tiller, 2004).The maximum contaminant level (MCL) established by United State Environmental Protection Agency (USEPA) for chromium is 0.05 mgl^{-1} as reported by Barakat 2010.In view of toxicities associated with these heavy metal ions, their removal from industrial effluents has become one of the thrust areas in modern research. The removal of Cr^{6+} from wastewater is accomplished by various conventional techniques like precipitation with hydroxide ion or lime (Ehrampoush *et al*., 2015), ion exchange (Sandeep, 2015), coagulation (Wang and Chen, 2009), electrochemical process (Sandeep, 2015), reverse osmosis and ion flotation (Kong *et al*., 2014). But these conventional methods are very slow, generate toxic sludge, have poor efficiency, require continuous input of chemicals and involve high cost. Adsorption has become one of the alternative treatments, in recent years; the search for low-cost adsorbents that have metal-binding capacities has intensified (Barakat, 2010). The adsorbents may be of mineral, organic or biological origin, zeolites, industrial byproducts, agricultural wastes, biomass, and polymeric materials (Kurniawan *et al.*, 2005). Biosorption of heavy metals from aqueous solutions is a relatively new process that has proven very promising in the removal of contaminants from aqueous effluents (Dhir and Kumar, 2010). In recent years, various natural adsorbents such as agricultural wastes including sunflower stalks, *Eucalyptus* bark, maize bran, coconut shell, waste tea, rice straw, tree leaves, peanut, walnut husks, sesame husk among others have been tried to achieve effective removal of various heavy metals (Demirbas, 2008; Kahraman*et al*., 2008; Nameni*et al*., 2008). In view of this research, rice husk and corn cobs as one of the most abundant agricultural wastes will be used as an adsorbent in heavy metal removal from tannery effluent.Maize is a popular cereal crop cultivated in many parts of the world (Morris *et al.,* 2011). During the processing and production of corn, several wastes are generated including corn cobs and corn husk. The world production of corn increased in the 1980s, which also implies a high amount of corn cob waste. In Nigeria corn production increased from 4-11million tons from 2000-2018 (USDOA, 2019). It is estimated that about 18kg of cobs are obtained from every 100kg of corn produced (Kaźmierczak *et al.,* 2013). The corn cobs are regarded as carbonaceous materials but a greater percentage of it in Nigeria ends up in landfills as waste. Rice husk is an agro-waste which is produced as a by-product of rice milling industry and it is estimated to be more than 100 million tons with about 96 percent generated in developing countries (Ahile *et al.,* 2017), where Nigeria produced about 5 million tons in 2018 (USDOA, 2018). The use of rice husk as potential biosorbent for metal remediation and environment management technologies has increased in recent past due to its easy availability, low cost, reusability, high efficiency, easy processing, application and recovery without any adverse impact on the environment. Some more advantages associated with rice husk are its high adsorption even with low metal concentrations no additional nutrients requirements, easy operation, its strong affinity and high selectivity towards heavy metals which is because of the presence of binding groups on its surface (Sandeep, 2015). Hence, the objective of this paper was to evaluate the utilization of base (BMOD) and acid (AMOD) modified rice husk-corncobs composite for removal of chromium (VI) ion in simulated tannery wastewater.

MATERIALS AND METHODS

Sample collection and pretreatment: Fresh rice husk was obtained from a local rice mill in Bauchi, Bauchi state Nigeria. The impurities in rice husk were first pick out, then the rice husk was washed thoroughly with distilled water to remove adhering soil and clay before oven drying at 60◦C until a constant weight is attain, the sorbent obtained (hereafter raw rice husk). Corncobs were collected from a road side in Bauchi, Bauchi state Nigeria. The obtained raw materials were first hand picking the impurities and remove the remains of the corn on the straw. Wash with distilled water and sundry for 72 hours. The dried corncobs were then cut down, grind and sieve to obtain a fine powder of particle size of ≤ 212 μm. The processed Rice husk and Corn cobs powder were pre-treated separately with 6N HCl (acid treatment) and 1N NaOH (alkaline treatment) for 1h and the pretreated samples were filtered, washed thoroughly with distilled water until a clear mixture were obtained (i.e. turbidity free). The water layer in each case was decanted and the pretreated Rice husk and Corn cobs powder were dried in an oven at 50ºC for 24 h and weighed to constant weight.

Characterization of the adsorbent: The adsorbent was characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM) and Energy-disperse X-ray (EDX). The functional groups present in the adsorbent before and after treating the tannery effluent was determined by FTIR (NicoletTM 6700). Surface morphology was observed by SEM (JSM-6490LV, manufactured by JEOL, Japan) micrographs and the elemental composition by EDX. Further, the phase was identified by XRD.

Preparation of synthetic solutions (mimicking a typical tannery industrial effluent): Analytical grade reagents were used in preparing stock solutions from which the working solutions was obtained by diluting to required concentration. The stock solution of the metallic salt was prepared by dissolving 3.250g of CrO_3 in 1000 cm^3 of distilled water.

Experimental Design: The experiment was designed using Design Expert Software (Version 6.0.8) whereby the effect of adsorbent dosage, pH and contact time on the heavy metal ions sorption onto blended adsorbent was studied. The response surface methodology (RSM) technique involving central composite design (CCD) was utilized to optimize the three main sorption parameters selected, to achieve maximum ion removal. Table 1 shows the experimental range of the independent variables. The experimental data matrix was determined using Design Expert v6.0.8 and the obtained models were statistically analyzed using analysis of variance (ANOVA).

Table 1: 2-Level, 3-Factor experimental Design

Name	Unit	-level	+level
Adsorbent Dosage	g	1	6
pH		3	9
Contact Time	min	30	180

Source: Kumar and Gausar, 2011; feng et al., 2011 and Naiya et al., 2009

Batch adsorption experiment: All adsorption tests were carried out in 250mL conical flask containing 100mL of the tannery effluent. The tests were conducted by varying three factors, pH, contact time and adsorbent dosage, on Cr^{+6}biosorption. All the samples were agitated at 150 rpm at room temperature in orbital Shaker (Protech model 722). Samples were collected at the predetermined time interval of 30, 105, 180 and 230 min, respectively and filtered through filter paper (Whatman No.1 0.45µm). The filtrates were examined for metal ion concentration using the Atomic Absorption Spectrometer (AAS). The amount of metal ion adsorbed (q_e) and the percent removal (*%R*) were calculated using equations 1 and 2, respectively.

$$qe = V\frac{Co - Ce}{m} \quad (1)$$

$$\%R = \frac{Co - Ce}{Co} * 100 \quad (2)$$

Where qe is the amount of metal ion adsorbed (mg/g), C_o and C_e are the initial and equilibrium liquid-phase concentrations of the metal ion (mg/L) respectively, V is the volume of the solution (L) and m is the weight of the adsorbent used (g).

RESULT AND DISCUSSIONS

Characterization of the Adsorbent: *SEM-EDX analysis:* The surface morphology of the chemically treated Rice husk and Corn cob blended biosorbent before and after the biosorption were investigated using SEM. Plate 1-12 shows the surface morphology of chemically treated Rice husk and Corn cob blended biosorbent before and after the biosorption of Cr (VI) ion for both the acid modified (AMOD) and base modified (BMOD). The morphological characterization of chemically treated Rice husk and Corn cob blended biosorbent after the biosorption of Cr (VI) ion was significantly different from those before biosorption. The pores on the biomass surface became smooth after the biosorption. This change can be explained by accumulation of metal ion on the surface by electrostatic attraction effect, which has been reported previously by Peng *et al.* (2018).The EDX analysis showed the biosorbent surface elemental composition before and after the biosorption and the result is demonstrated in figure 1-4. The presence of Cr (VI) (Wt conc. = 0.42 and 0.63) on the surface of the biomass after biosorption confirmed the attachment of the metal ion on the biosorbent surface. It was observed that amount of N, Si, Cl, Al, Na, S, Mg, P, K, Fe and Ca decreased after the biosorption process. This change demonstrates a possible ion exchange has occurred during the biosorption of Cr (VI) ion. Similar observations were reported by Oliveira *et al.,* (2014).Elemental mapping was carried out to show the spatial distribution of each element detected in EDX (Figures 1-4).

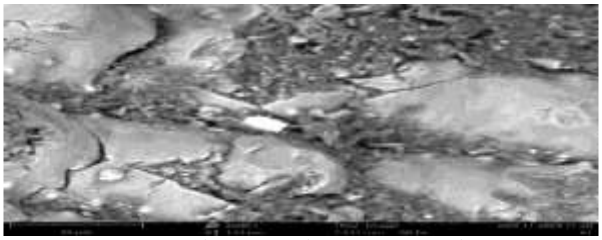

Plate 1: SEM image of AMOD before biosorption of Cr (VI) ion, 30µm

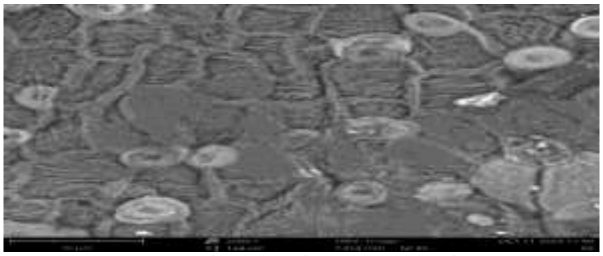

Plate 2: SEM image of AMOD after biosorption of Cr (VI) ion, 30µm

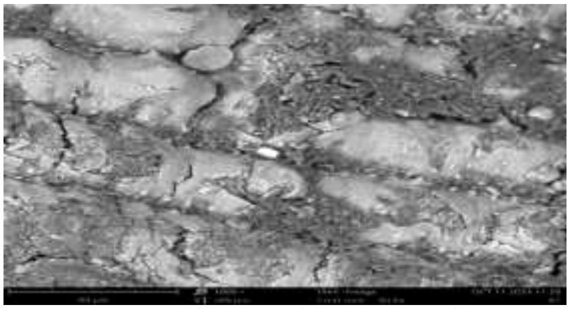
Plate 3: SEM image of AMOD before biosorption of Cr (VI) ion, 80μm

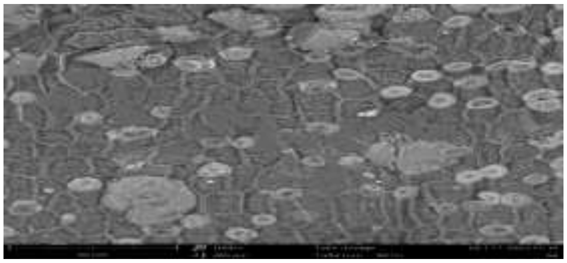
Plate 4: SEM image of AMOD after biosorption of Cr (VI) ion, 80μm

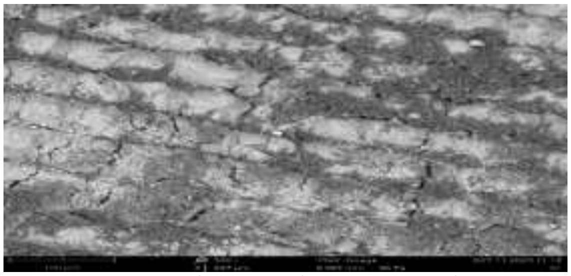
Plate 5: SEM image of AMOD before biosorption of Cr (VI) ion, 100μm

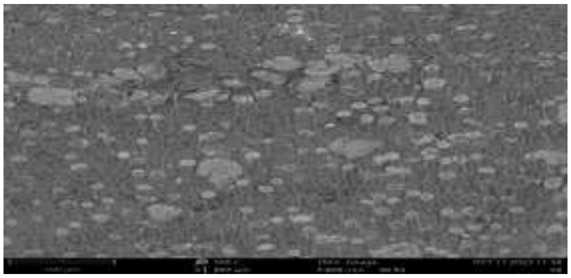
Plate 6: SEM image of AMOD after biosorption of Cr (VI) ion, 100μm

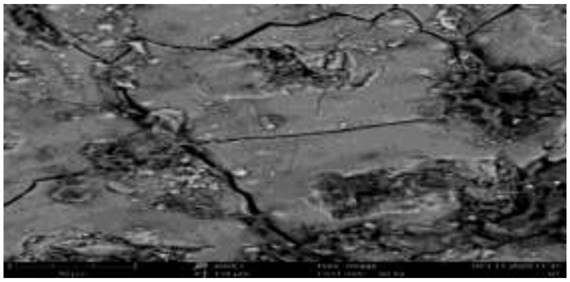
Plate 7: SEM image of BMOD before biosorption of Cr (VI) ion, 30μm

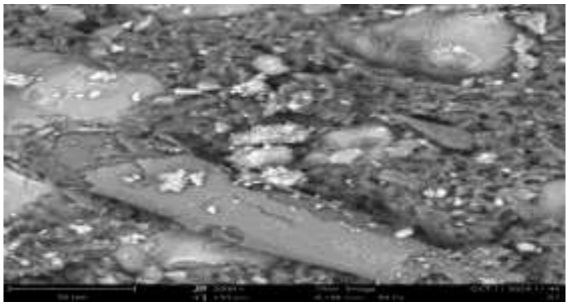
Plate 8: SEM image of BMOD after biosorption of Cr (VI) ion, 30μm

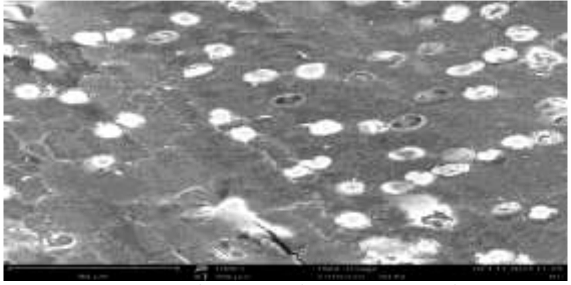
Plate 9: SEM image of BMOD before biosorption of Cr (VI) ion, 80μm

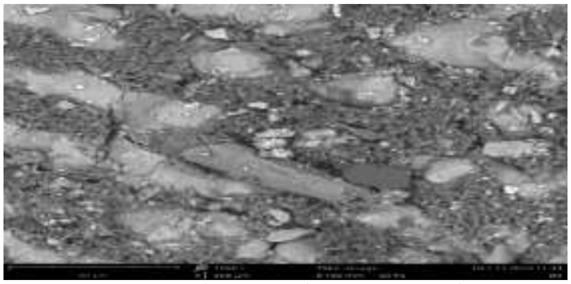
Plate 10: SEM image of BMOD before biosorption of Cr (VI) ion, 100μm

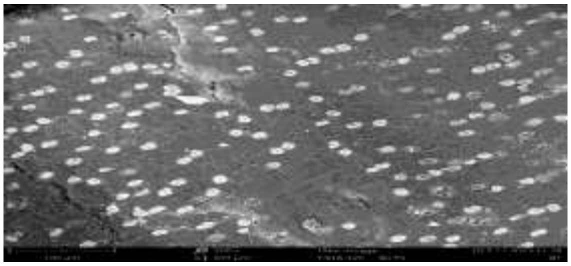
Plate 11: SEM image of BMOD after biosorption of Cr (VI) ion, 80μm

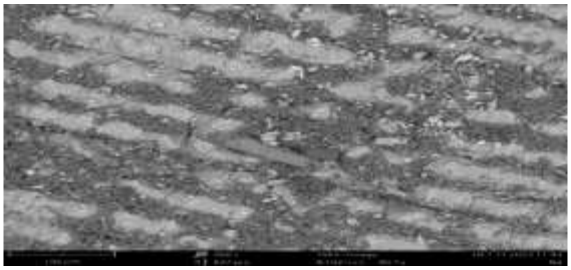
Plate 12: SEM image of BMOD before biosorption of Cr (VI) ion, 100μm

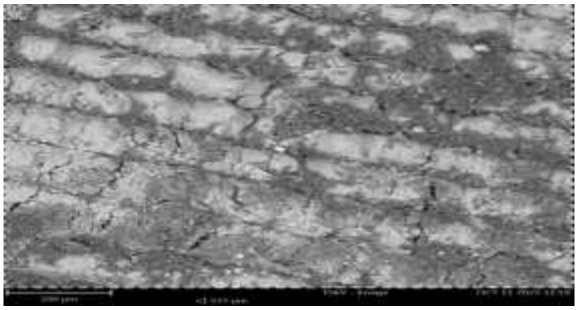

Plate 13: Energy-dispersive X-ray (EDX) spectrums for acid modified (AMOD) before biosorption of Cr (VI) ion

Table 2: Elemental Composition from the Energy-dispersive X-ray (EDX) spectrums for acid modified (AMOD) before biosorption of Cr (VI) ion.

Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
6	C	Carbon	71.03	59.06
14	Si	Silicon	11.10	21.59
7	N	Nitrogen	16.02	15.53
13	Al	Aluminium	0.42	0.79
11	Na	Sodium	0.48	0.76
20	Ca	Calcium	0.14	0.38
19	K	Potassium	0.13	0.36
16	S	Sulfur	0.16	0.36
17	Cl	Chlorine	0.14	0.34
12	Mg	Magnesium	0.19	0.32
15	P	Phosphorus	0.13	0.29
26	Fe	Iron	0.06	0.22

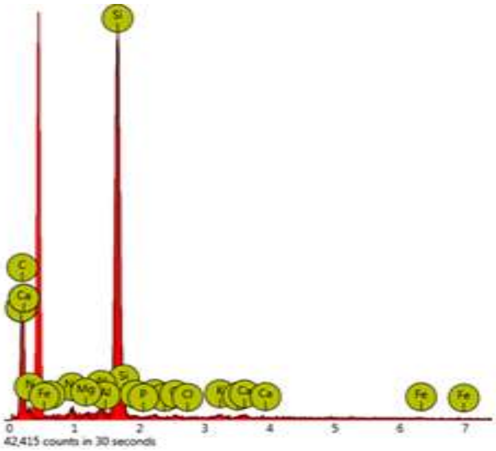

Fig 1: Elemental mapping from the Energy-dispersive X-ray (EDX) spectrums for acid modified (AMOD) before biosorption of Cr (VI) ion.

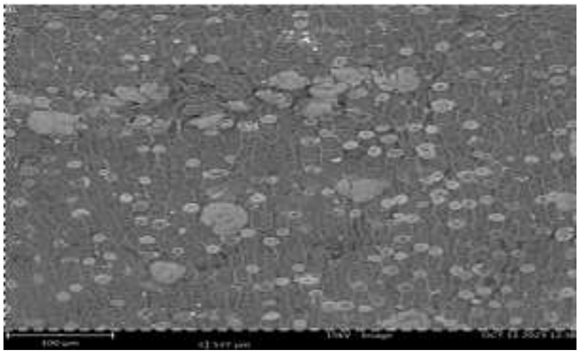

Plate 14: Energy-dispersive X-ray (EDX) spectrums for acid modified (AMOD) after biosorption of Cr (VI) ion.

Table 3: Elemental Composition from the Energy-dispersive X-ray (EDX) spectrums for acid modified (AMOD) after biosorption of Cr (VI) ion.

Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
6	C	Carbon	81.14	74.77
7	N	Nitrogen	13.16	14.14
11	Na	Sodium	3.44	6.07
14	Si	Silicon	1.30	2.80
12	Mg	Magnesium	0.26	0.48
13	Al	A,uminium	0.20	0.41
24	Cr	Chromium	0.17	0.42
17	Cl	Chlorine	0.15	0.40
19	K	Potassium	0.10	0.31
16	S	Sulfur	0.11	0.27
15	P	Phosphorus	0.10	0.23
20	Ca	Calcium	0.04	0.11
26	Fe	Iron	0.00	0.00

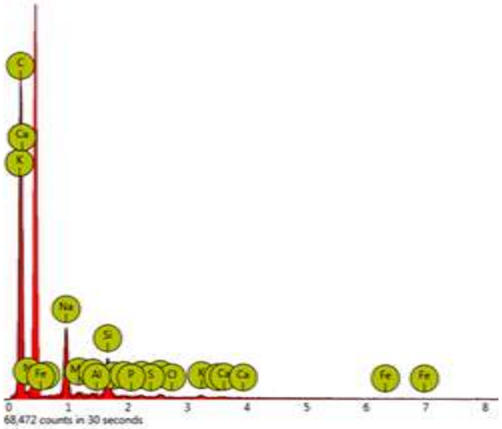

Fig.2: Elemental mapping from the Energy-dispersive X-ray (EDX) spectrums for acid modified (AMOD) after biosorption of Cr (VI) ion.

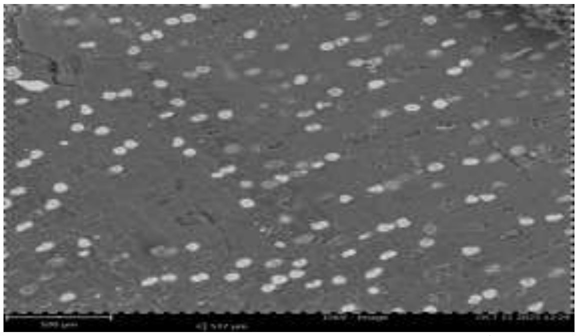

Plate 15: Energy-dispersive X-ray (EDX) spectrums for base modified (BMOD) before biosorption of Cr (VI) ion

Table 4: Elemental Composition from the Energy-dispersive X-ray (EDX) spectrums for base modified (BMOD) before biosorption of Cr (VI) ion

Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
6	C	Carbon	83.92	79.43
7	N	Nitrogen	13.65	15.07
14	Si	Silicon	1.28	2.84
17	Cl	Chlorine	0.25	0.69
13	Al	Aluminium	0.21	0.44
11	Na	Sodium	0.22	0.39
16	S	Sulfur	0.14	0.36
12	Mg	Magnesium	0.18	0.35
15	P	Phosphorus	0.10	0.24
19	K	Potassium	0.04	0.11
26	Fe	Iron	0.02	0.09
20	Ca	Calcium	0.00	0.00

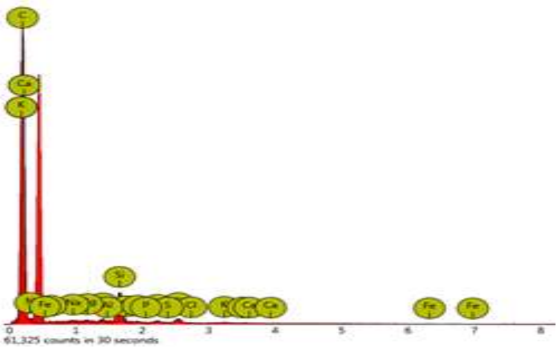

Fig. 3: Elemental mapping from the Energy-dispersive X-ray (EDX) spectrums for base modified (BMOD) before biosorption of Cr (VI) ion.

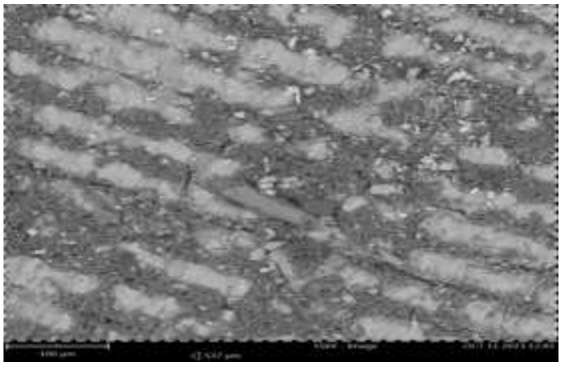

Plate 16: Energy-dispersive X-ray (EDX) spectrums from the base modified (BMOD) after biosorption of Cr (VI) ion.

Table 5: Elemental Composition from the from the Energy-dispersive X-ray (EDX) spectrums for base modified (BMOD) after biosorption of Cr (VI) ion.

Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
6	C	Carbon	71.11	59.53
14	Si	Silicon	9.58	18.76
7	N	Nitrogen	17.02	16.62
20	Ca	Calcium	0.37	1.05
15	P	Phosphorus	0.47	1.01
13	Al	Aluminium	0.46	0.87
24	Cr	Chromium	0.32	0.63
17	Cl	Chlorine	0.22	0.55
11	Na	Sodium	0.31	0.50
26	Fe	Iron	0.11	0.42
16	S	Sulfur	0.14	0.32
12	Mg	Magnesium	0.17	0.29
19	K	Potassium	0.03	0.07

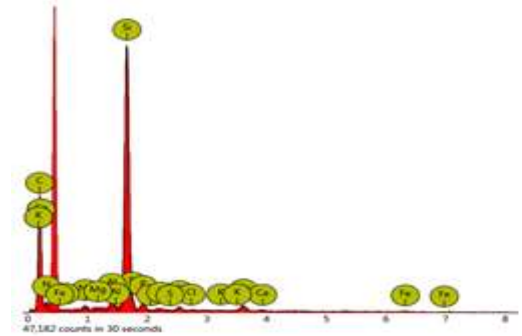

Fig. 4: Elemental mapping from the Energy-dispersive X-ray (EDX) spectrums for base modified (BMOD) after biosorption of Cr (VI) ion.

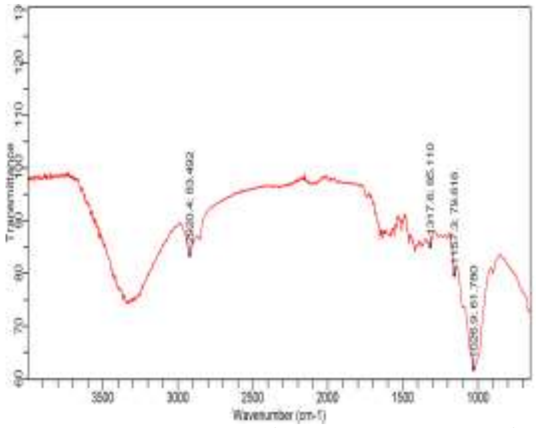

Fig 5: FTIR pattern acid modified (AMOD) biosorbent before biosorption of Cr (VI)) ion

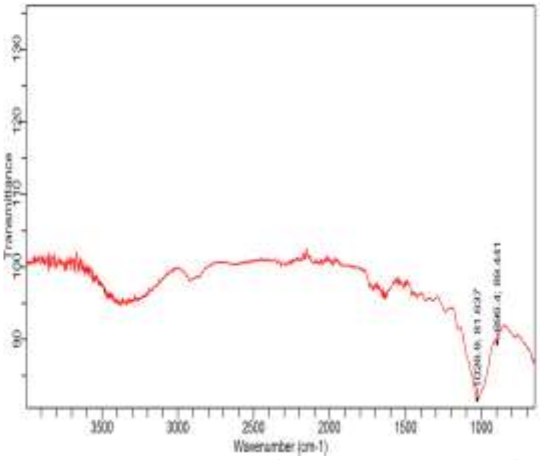

Fig 6: FTIR pattern base modified (BMOD) biosorbent before biosorption of Cr (VI)) ion

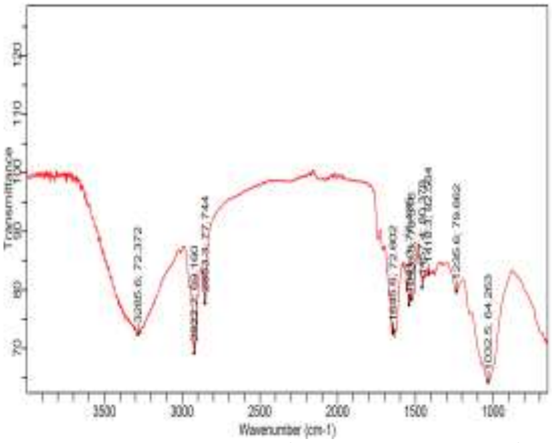

Fig 7: FTIR pattern acid modified (AMOD) biosorbent after biosorption of Cr (VI)) ion

FTIR analysis: The functional groups on the biosorbent surface and their interaction during the biosorption process of Cr (VI) ion was investigated through FTIR spectrum analysis. Figure 5-8 shows the peaks corresponding to the functional groups of biosorbent before and after the biosorption of metal ion.

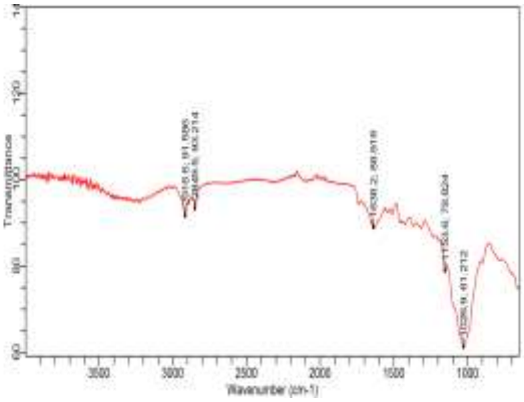

Fig 8: FTIR pattern base modified (BMOD) biosorbent after biosorption of Cr (VI)) ion

The broad and strong peak at 3285.6 cm^{-1} was assigned to the overlapping of O–H and N–H stretching, indicating the existence of hydroxy stretching and carboxylic groups on the surface on biosorbent (Mubeen *et al.*, 2019). The peaks at 2922.2, 2853.3 and 1645.6 cm^{-1} respectively were attributed to the C–H stretching vibration of aliphatic groups and at 1541.3 cm^{-1} was attributed to the presence of C=O stretching. The peak at 1457.4 cm^{-1} represented the presence of C=C stretching. The peak found at 1418.3 cm^{-1} was assigned to the C–H bonding. The peaks observed at 1235.6, 1157.3 and 1153.6 cm^{-1} were attributed to the C–O stretching. The sulfoxide band was assigned to the peaks observed at 1032.5 and 1026.9 cm^{-1}. The numerous characteristic peaks observed on the surface indicate the complex nature of the biosorbent. Table 2 shows changes in the vibrational frequency of the functional groups after the biosorption of Cr (VI) ions on both AMOD and BMOD biosorbent. This indicates the biosorption of Cr (VI) ion on the biosorbent by chemical combination

Table 6**:** Infrared vibration wavenumber and functional groups observed on acid modified (AMOD) and base modified (BMOD) biosorbent

Wavenumber (cm^{-1})				Functional Groups
AMOD Unloaded	AMOD Loaded	BMOD Unloaded	BMOD Loaded	
1026.9;61.780	1032.5;64.263	1026.9;637	1026.9;61.212	C-O stretching
1157.3;79.616	1235.6;79.662	-	1153.6;78.824	C-O stretching
1317.6;85.110	1418.3;82.564	-	-	C-H stretching
-	1457.4;80.378	-	-	C=C stretching
-	1526.3;78.336	-	-	Asymmetric C=C stretching
-	1541.3;77.435	-	-	C=O stretching
-	1645.6;72.602	-	1638.2;88.918	C-H symmetric stretching
-	2853.3;77.744	-	2849.5;93214	C-H asymmetric stretching
2920.4;83.492	2922.2;69.160	-	2916.6;91.586	C-H stretching
-	3285.6;72.372	-		O-H stretching

Equilibrium Studies: The effect of pH: The effect of pH on the removal percentage of Cr (VI) ions from Tannery effluent using acidified (AMOD) and basic modified (BMOD) biosorbents as shown in figure 9 is significant. For acidified modified (AMOD) biosorbents, the removal efficiency ranges from 87.8% at pH 1 to 97.9% at pH 9, with the highest efficiency observed at pH 9.

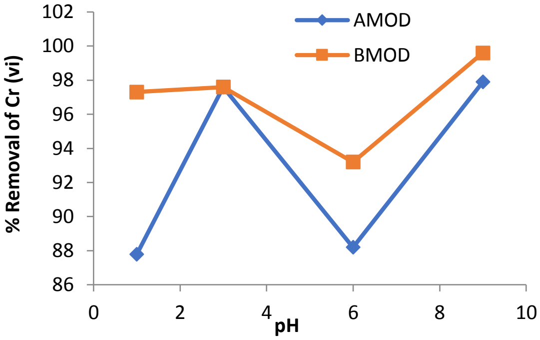

Fig 9: Effect of pH on Cr (VI) ion removal for acidified modified (AMOD) and base modified (BMOD) biosorbent

In contrast, basic modified (BMOD) biosorbents exhibit removal efficiencies from 97.3% at pH 1 to 99.6% at pH 9, with the highest efficiency at pH 9. Overall, the data highlights that pH plays a crucial role in the adsorption process, affecting the removal efficiency by influencing the surface charge of the biosorbents and the speciation of Cr (VI) ions. Optimal removal efficiency is achieved at slightly acidic to alkaline pH levels (pH 3 to pH 9) for both acidified modified (AMOD) and basic modified (BMOD) biosorbents.

Effect of Adsorbent dosage: From Fig. 10, the Effect of Adsorbent Dosage on the removal percentage of Cr (VI) ions using acidified modified (AMOD) and base modified (BMOD) biosorbents in Tannery effluent shows that increasing the biosorbent dosage enhances removal efficiency. Specifically, at an Adsorbent Dosage of 1, the removal percentage of Cr(VI) ions is 86.2%, indicating moderate efficiency. Increasing the Dosage to 3.5 significantly enhances removal efficiency to 99.5%. At a Dosage of 6, the removal percentage remains high at 96.3%, showing consistent efficiency. Finally, with a Dosage of 7.7, the removal percentage reaches 98.1%, indicating high efficiency at this higher dosage level. Overall, the data suggests that increasing the Biosorbent dosage improves the removal efficiency of Cr(VI) ions, with the highest efficiency observed at a dosage of 3.5.

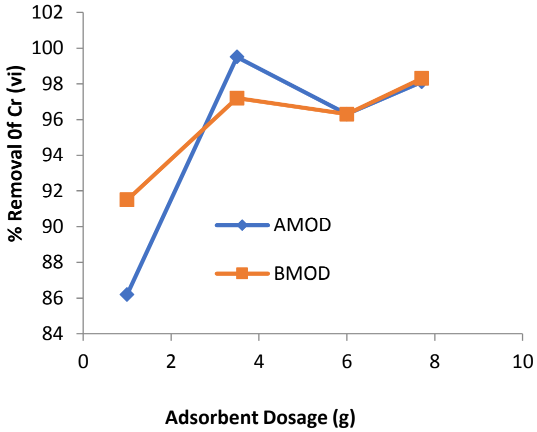

Fig 10: Effect of Adsorbent dosage on Cr (VI) ionremoval for acidified modified (AMOD) and base modified (BMOD) biosorbent.

Effect of Contact Time: The impact of Contact Time on the removal efficiency of Cr(VI) ions using acidified modified (AMOD) biosorbents in Tannery effluent is evident from the data in figure 11. Initially, at 20 minutes, the removal efficiency is 88.2%, indicating moderate effectiveness.

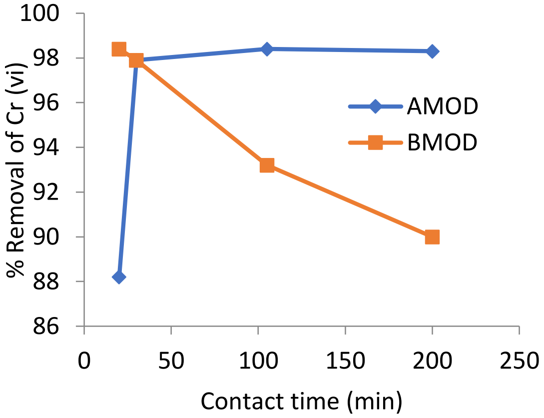

Fig 11: Effect of contact time on Cr (VI) ion removal for acidified modified (AMOD) and base modified (BMOD) biosorbent.

Subsequently, increasing the contact time to 30 minutes notably enhances the removal efficiency to 97.9%. The peak efficiency is observed at 105 minutes, reaching 98.4%, demonstrating high effectiveness at this duration. Maintaining a high level, even at 200 minutes, the removal efficiency remains at 98.3%. Overall, the data suggests that extending the contact time improves the removal efficiency of Cr(VI) ions, with optimal efficiency seen at 105 minutes. In contrast, for base modified (BMOD) biosorbents in the effluent, the removal percentage of Cr(VI) ions decreases as the contact time increases. Starting at 98.4% at 20 minutes, the removal efficiency declines to 90% at 200 minutes, indicating a reduction in efficiency over time.

Model Development for Cr (VI) ion Removal: A CCD matrix was used to investigate the interaction effects of three important factors, including adsorbent dosage, contact time, and pH, on the removal of Cr (VI) ion. The experimental design and the responses are shown in Table 3. Based on the obtained results, the following polynomial equation was developed for Cr (VI) ion removal for the acid modified (AMOD) and no model equation was developed for the base modified (BMOD) biosorbent which suggested that the heavy metal ion concentration is low or the efficiency of the biosorbent is high as such the percentage removal is very closed.

$$\begin{aligned} Cr(VI)\ Removeval\ \% \\ &= +91.19 + 1.71A + 1.21B \\ &- 0.50C + 1.26A^2 + 0.12B^2 \\ &+ 2.61C^2 - 1.24AB \end{aligned}$$

Where A, B, and C are the coded values for the selected influential parameters, namely, adsorbent dosage, pH and contact time, respectively.

Table 7: Experimental design for biosorption of Cr (VI) ion on acid modified (AMOD) biosorbent. CCD: central composite design.

Run	Independent Factors			Responses
	Adsorbent Dosage	Contact Time	pH	Cr (VI) ion Removal%
1	6.00	30.00	9.00	97.9
2	3.50	200.00	6.00	98.3
3	3.50	105.00	6.00	99.5
4	6.00	30.00	3.00	98.9
5	3.50	105.00	11.00	94.1
6	7.70	105.00	6.00	98.1
7	3.50	105.00	6.00	98.4
8	3.50	105.00	6.00	99.6
9	1.00	180.00	3.00	87.5
10	1.00	105.00	6.00	86.2
11	6.00	180.00	9.00	94.3
12	3.50	105.00	1.00	87.8
13	1.00	30.00	3.00	97.6
14	1.00	30.00	9.00	96
15	6.00	180.00	3.00	95.3
16	3.50	105.00	6.00	83.2
17	3.50	20.00	6.00	88.2
18	3.50	105.00	6.00	79.2
19	1.00	180.00	9.00	97
20	3.50	105.00	6.00	92.6

Table 4 shows the ANOVA for the polynomial equations and the corresponding regression coefficients for the removal models of Cr (VI) ion The significance of the obtained models can be determined based on the p-value, the correlation of determination (R^2), and the results of the lack of fit test (Zhu X., *et al.*, 2017). Both models showed p-values (Prob > F) greater than 0.0500, suggesting their not significant.

The lack of fit test showed the variation of responses around the fitted model. The insignificant lack of fit indicated that the model did not fit the data well. The values of R^2 and adjusted R^2 were 0.2146 and -0.2436. The coefficient of variance (CV) refers to the ratio of standard deviation to mean. The CV value was 7.19. A model is reproducible if the CV value is less than 10 (Haftu, 2015). Adequate precision (AP) is defined as the ratio of signal to noise. An AP ratio higher than 4 is desired. The AP value of the model was 1.907, which indicates an inadequate signal and we should not use this model to navigate the design space.

Adsorption Kinetic Study: In this study, three different kinetics models were investigated, namely the pseudo-first order, the pseudo-second order, and the Elovich kinetic models, to test the experimental data.

The parameters for each kinetic model and its respected correlation coefficients (R^2) are shown in Table 5. Plots of the three kinetic models are shown in Figure 12-14 for both the acid modified (AMOD) and base modified (BMOD) composite biosorbent. The experimental results fitted well with the pseudo-second order model for both acid modified (AMOD) and base modified (BMOD) with R^2 values of 0.6900 and 0.6840 respectively.

Adsorption Isotherm Study: The sorption equilibrium data were tested with two parameter models: Langmuir and Freundlich isotherms. The model parameters for each isotherm, their respected correlation coefficients (R^2) values are shown in Table 6. Figure 15-16 illustrates the Langmuir and Freundlich adsorption isotherms of ions on the biosorbent.

Table 8: Analysis of variance (ANOVA) for Cr (VI) ion biosorption model on AMOD biosorbent.

Response	**Source**	**Sum of squares**	**df**	**Mean Square**	**F Value**	**p-Value Prob>F**	**Comments**
Cr (VI) ion Removal (%)	Model	148.21	7	21.17	0.47	0.8396	SD= 6.72
	A	30.72	1	30.72	0.68	0.4258	Mean=93.48
	B	19.84	1	19.84	0.44	0.5202	CV=7.19
	C	2.67	1	2.67	0.059	0.8120	R^2=0.2146
	A^2	13.56	1	13.56	0.30	0.5939	$R^2_{(Adj)}$=-0.2436
	B^2	0.20	1	0.20	4.394E-003	0.9482	AP=1.907
	C^2	40.28	1	40.28	0.89	0.3639	
	AB	12.25	1	12.25	0.27	0.6121	
	Residual	542.53	12	45.21			
	Lack of Fit	145.96	7	20.85	0.26	0.9448	
	Pure Error	396.57	5	79.31	0.47	0.8396	

s: significant; n: insignificant; df: degree of freedom; SD: standard deviation; CV: coefficient of variance; R^2: correlation of determination; AP: adequate precision

Table 9: The Pseudo-first order, Pseudo-second order And Elovich kinetic parameters for biosorption of Cr (VI) ion onto Composite biosorbent.

Model	Equation	Parameters	AMOD Cr(VI) ion	BMOD Cr(VI) ion
Pseudo-first order	$\log(q_e - q_t) = \log(q_e) + k_1 t$	q_e (mg/g)	1.0217	1.0414
		k_1 (1/min)	0.00004	0.0002
		R^2	0.0010	0.0440
Pseudo-second order	$\frac{t}{q_t} = \frac{1}{q_e k_2} + \frac{1}{q_e} t$	q_e (mg/g)	0.7131	0.9825
		k^2 (g/(min.mg))	0.3079	-0.1862
		R^2	0.6900	0.6840
Elovich kinetic model	$q_t = \frac{1}{\beta} \ln \alpha\beta + \frac{1}{\beta} \ln t$	A	-5.730×10^{-8}	-1.303×10^{-5}
		B	-3.6887	-31.250
		R^2	0.0521	0.0470

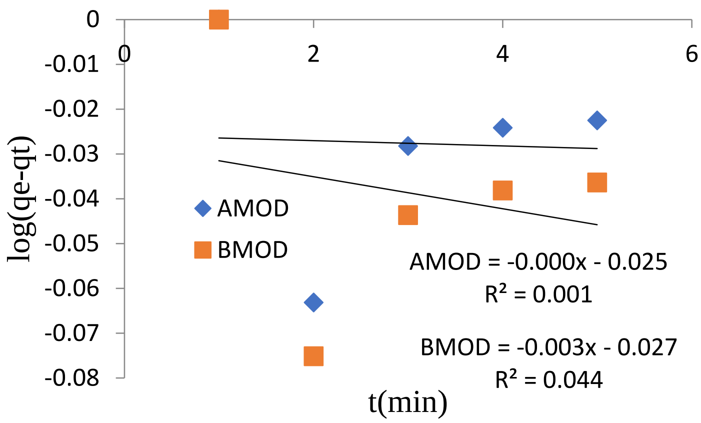

Fig 12**:** Linear fitting of biosorption of Cr (VI) ion by acid modified (AMOD) and base modified (BMOD) Compositesbiosorbent to the pseudo-first order kinetic models.

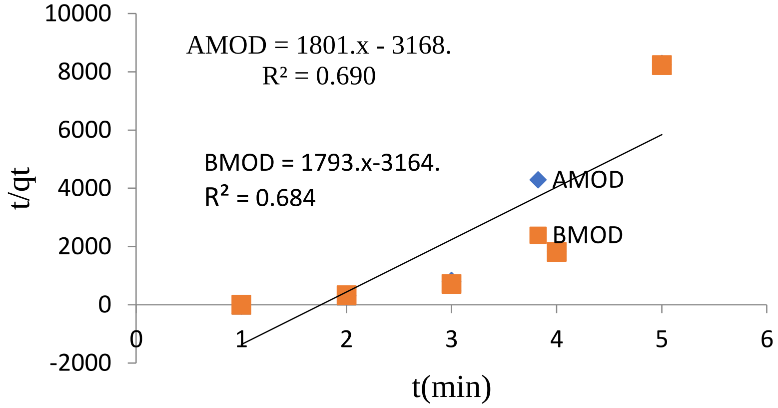

Fig 13**:** Linear fitting of biosorption of Cr (VI) ion by acid modified (AMOD) and base modified (BMOD) Composites biosorbent to the Pseudo-second order kinetic models.

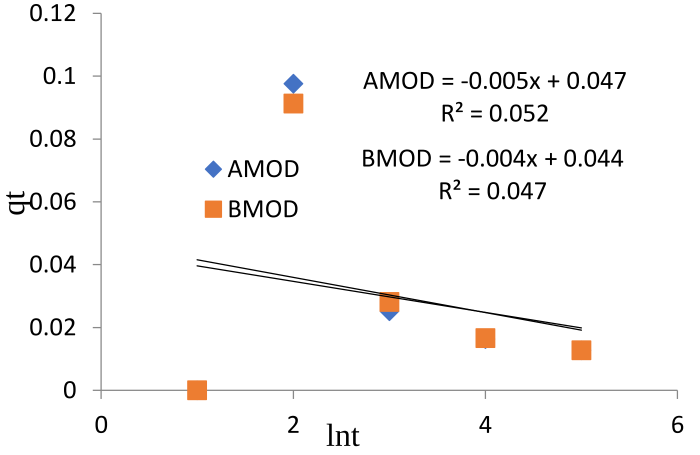

Fig 14**:** Linear fitting of biosorption of Cr (VI) ion by acid modified (AMOD) and base modified (BMOD) Composites biosorbent to the Elovich kinetic models

Table 10: Isotherm constants for Cr (VI) ion biosorption onto Composite biosorbent.

Heavy metals	**Langmuir Isotherm Coefficient**				**Freundlich Isotherm Coefficient**		
	q_o(mg/g)	b (L/mg)	R^2	R_L	K_F [(mg/g)/(L/mg)]$^{1/n}$	1/n	R^2
AMOD	1.5466	-0.1048	0.115	-0.0529	2.5276	0.0402	0.8520
BMOD	0.6748	-0.0508	0.234	-0.1707	6.7391	-0.3943	0.8560

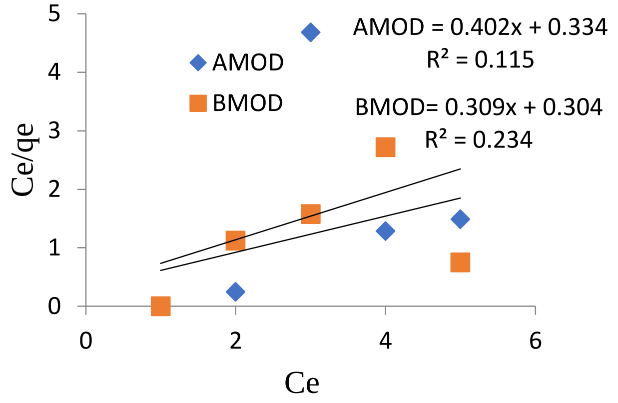

Fig 15: Langmuir isotherm plot for Cr (VI) ion sorption onto acid modified (AMOD) and base modified (BMOD) Composites.

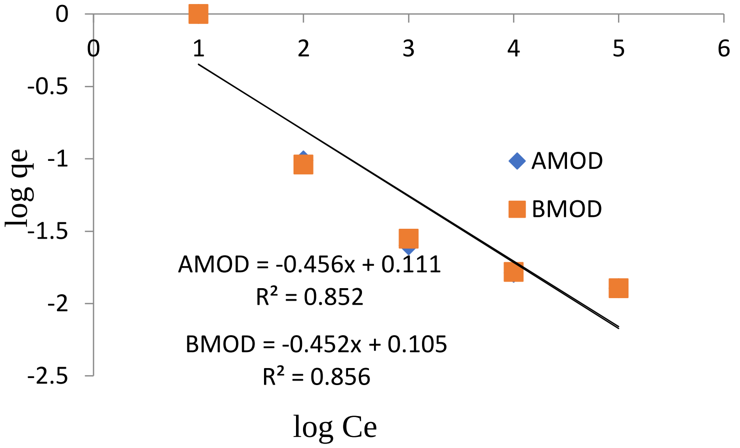

Fig 16: Freundlich isotherm plot for Cr (VI) ion sorption onto acid modified (AMOD) and base modified (BMOD) Composites.

Conclusion: The study has demonstrated that a composite of rice husk and corncobs is effective as a biosorbent for the removal of metal ions from industrial effluent. This development will benefit wastewater management in the tannery, textile and related industries. In conclusion, the results of the study indicate a definitive approach to addressing environmental concerns associated with the presence of heavy metal ions.

Declaration of Conflict of Interest: The authors declare no conflict of interest.

Data Availability Statement: Data are available upon request from the corresponding author

REFERENCES

Adam, F; Balakrishnan S; Wong, P. (2006). Rice husk ash silica as a support material for ruthenium based heterogeneous catalyst. *J Phy. Sci.* 17(2): 1-13.

Agrawal, A; Sahu, KK; Pandey, BD. (2005). Systematic studies on adsorption of lead on sea nodule residues, *J. Colloid Interface Sci.* (281) 291–298.

Ahile, UJ; Ama, SO; Mchihi, MM; Oteikwu, MO; Nyom, PN; Utange, PI. (2017). Removal of Pb^{2+} from aqueous solution using rice husk as an adsorbent. *FUW T Sci. Technol. J,* 2 (2) 886 – 889.

Ahmad T. (2010). Biooxidation and precipitation for iron and sulphate removal from heap bioleaching effluent streams Hydrometallurgy, *Inorg. Chem. J,* 1 (2) 7−14.

Ahmed MI. (2009). Cadmium adsorption on HDTMA modified montmorillonite, *J. Eng. Res.* 6 (1) 8-14

Ali I; Gupta VK (2007). Advances in water treatment by adsorption technology. *Nat Protoc* 1:266–2667

Alireza B; Mohammadi S; Mowlavi A; Parvaresh P (2010). Measurement of heavy radioactive pollution: radon and radium in drinking water samples in Mashhad. *Int. J Curr Res* 10:54–58

Amanial HR. (2015). Physico-chemical characterization of tannery effluent and its impact on the nearby river. *J. Environ. Chem. Ecotoxi*. Vol. 8(6), pp. 44-50.

Aroke UO; El-Nafaty UA; Osha, OA. (2014). Removal of Oxyanion Contaminant from Waste Water by Sorption onto HDTMA-Br Modified Organo-Kaolinite clay. North-Eastern, *Nig. Int. Emer. Technol. Adv. Eng.* 4 (1) 475-484.

Ashbolt NJ (2004). Microbial contamination of drinking water and disease outcomes in developing regions. Toxicology 198:229–238

Berndt H; Mo¨nnicha I; Lu¨cke B; Menzel M (2001). Tin promoted palladium catalysts for nitrate removal from drinking water. *Appl Catal B* 30:111–122

Bining, AS; Jenkins, BM (1992). Thermo chemical reaction kinetics for rice straw from an approximate integral technique. *American Society of Agricultural Engineers.Meeting* (USA). No. 92-6001/92-6040.

Bolognesi C (2003). Genotoxicity of pesticides: a review of human biomonitoring studies. Mutat Res 543:251–272 Bowe CA, Martin DF (2004) Extraction of heavy metals by 2-mercaptoethoxy group attached to silica gel. *J Environ. Sci Health Tox. Haz. Subst. Environ. Eng.* 39(6):1469–1485

Bowe CA; Poore DD; Benson RF; Martin DF (2003). Extraction of heavy metals by amine adsorbed onto silica gel. *J Environ. Sci Health Tox. Haz. Subst. Environ. Eng.* 38(11):2653–2660

Brown HS; Bishop DR; Rowan CA (1984).The role of skin absorption as a route of exposure for volatile organic compounds (VOCs) in drinking water. *Am J Pub Health* (AJPH) 74:5

Buljan J; Kral I. (2011); Introduction to treatment of tannery effluents.*United Nations Industrial Development Organization (UNIDO)* Vienna.

Charcosset C (2009). A review of membrane processes and renewable energies for desalination. Desalination 245:214–231

Chen W and Liu H. (2014) Adsorption of sulphate in aqueous solutions by organonanoclay: Adsorption equilibrium and kinetic studies, (1974-1981).

Chong MN; Jin B; Chow CWK; Saint C (2010). Recent developments in photocatalytic water treatment technology: a review. Water Res 44:2997–3027

Conradt, R; Pimkhaokham, P; Leela-Adisorn, U. (1992). Nanostructured silica from rice husk. *J. Non-Cry. Sol.*. 145: 75-79.

Cruz-Guzman, M; Celis, R; Hermosın, MC; Koskinen, WC; Nater, EA; Cornejo (2006). Heavy Metal Adsorption by Montmorillonites Modified with Natural Organic Cations. Soil Science Society of America (70)215–221.

Dabrowski, A. (2001). Adsorption from theory to practice, Adv. *Colloid Interface Sci*, (108) 135–224.

Damalas CA, Eleftherohorinos IG (2011) Pesticide exposure, safety issues, and risk assessment indicators. *Int J. Environ Res Public Health* 8:1402–1419

Demirbas, A. (2008). Heavy metal adsorption onto agro-based waste materials: A review. *J. Hazard. Mater*.157, 220-229.

Dentel, SK; Jamrah, AI. (1995). Selective adsorption of organic material from water by modified clays, US patent 5401417.

Dhir, B; Kumar, R. (2010). Adsorption of Heavy Metals by *Salvinia*Biomass and Agricultural Residues. *Int. J. Environ. Res., 4(3):427-432.*

Eikebrokk B; Juhna T; Østerhus SW (2006) Water treatment by enhanced coagulation—operational status and optimization issues.Techneau D 5(3):1

Environmental Protection Agency US (2000) Wastewater technology sheet: chemical precipitation. United State Environmental Protection, 832-F-00-018

Environmental Protection Agency, US (2006) Inorganic Contaminant Accumulation in Potable Water Distribution Systems, Office of Groundwater and Drinking Water, USA

Gaya UI; Abdullah AH (2008). Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: a review of fundamentals, progress and problems. *J PhotochemPhotobiol C Photochem* Rev 9:1–12

Gil A, Amiri MJ, Javad M, Abedi-Koupai J (2018) Adsorption/reduction of Hg(II) and Pb(II) from aqueous *solutions by using bone ash/nZVI composite: effects of aging time, Fe loading quantity and co-existing ions. Environ Sci Pollut Res* 25:2814–2829.

Gimbert, F., Morin-Crini, N., Renault, F., Badot, P.M. and Crini, G. (2008). Adsorption isotherm models for dye removal by cationized starch-based material in a single component system: error analysis. (20) (34–46).

Govindarao, V. M., 1980. Utilization of rice husk.A preliminary analysis.*J. of Sci. and Ind Res.* 39(9): 495-515.

Gunay, A.E. Arslankaya I. T, (2007). Lead removal from aqueous solution by natural and pre-treated clinoptilolite: adsorption equilibrium and kinetics. (14) 362–371.

Hameed, B. H., Mahmoud, D. K. and Ahmad, A. L., (2008). Equilibrium modeling and kinetic studies on the adsorption of basic dye by a low-cost adsorbent: Coconut (Cocos nucifera) bunch waste. *J. Haz. Mater*., 158(1) 65-72.

Harvey RW; Smith RL; George L (1984). Effect of organic contamination upon microbial distributions and heterotrophic uptake in a Cape Cod, Mass., aquifer. *Appl. Environ.Microb.* 48(6):1197–1202

Heasman M; Mellentin J (2001). The functional foods revolution healthy people, healthy profits. Earthscan Publisher, London, p 280. ISBN 978-1-85383-687-9

Heckel A, Seebach D (2000). Immobilization of TADDOL with a high degree of loading on porous silica gel and first applications in enantioselective catalysis. *Angew. Chem. Int. Ed.* 39(1):163–165

Hitzfeld BC, Ho¨ger SJ, Dietrich DR (2000) Cyanobacterial toxins: removal during drinking water treatment, and human risk assessment. *Environ Health Perspect* 108:113–122

Ho, Y. S., (2006). Review of second-order models for adsorption systems. *J. Haz. Mater*, 136(3), pp. 103-111.

Ho, YS; Mckay, G. (1998a). A comparison of chemisorption kinetic models applied to pollutant removal on various sorbents. Process Safety and Environmental Protection, 76(4), pp. 332-340.

Ho, YS; Porter JF; Mckay G., (2002) Equilibrium isotherm studies for the sorption of divalent metal ions onto peat: copper, nickel and lead single component systems, *Water Air Soil Pollut* 3 (2) 1–33.

Ibhadon AO; Fitzpatrick (2013). Hetergeneousphotocatalysts; recent advances and applications. Catalysts 3:189–218

Iler R.K (1979). The chemistry of silica. Wiley, New York

Inamori Y; Fujimoto N (2009) Water quality and standards—Vol. II, microbial/biological contamination of water. Encyclopaedia of Life support systems (EOLSS)

Jafarpour MM; Foolad A; Mansouri MK; Nikbakhsh Z; Saeedizade H (2010). Ammonia removal from nitrogenous industrial waste water using Iranian natural zeolite of clinoptilolite type. *World Acad Sci Eng. Technol* 46:939–945

Jiuhui QU (2008) Research progress of novel adsorption processes in water purification: a review. *J. Environ. Sci.* 20(1):1–13

Joseph, K. M., Solomon, G. A., Julius, N. N. and Adélaïde, M. K. (2011). Kinetic and equilibrium studies of the adsorption of lead (II) ions from aqueous solution onto two Cameroon clays: Kaolinite and smectite, *J. Environ. Chem. Ecotox.* 3(11) 290-297.

Joseph, KR; Toledo, B; James, S. Thomas, S; Carvalho, LH. (1999). A review on sisal fiber reinforced polymer composites. RevistaBrasileira de Engenharia Agricola Ambiental. 3 (3): 367–379.

Kahraman, S., Dogan, N. and Erdemoglu, S. (2008). Use of various agricultural wastes for the removal of heavy metal ions. *Intnl.J. Environ. Pollut*.34, 275-284.

Kallo´ D (2001). Applications of natural zeolites in water and wastewater treatment. Rev Min Geochem 45:519–550

Karapınar N (2009) Application of natural zeolite for phosphorus and ammonium removal from aqueous solutions. *J Hazard Mat* 170(2–3):1186–1191

Kaźmierczak, J. Nowicki P. &Pietrzak, R. (2013) “Sorption properties of activated carbons obtained from corn cobs by chemical and physical activation", Adsorption, 19: 273- 281.

Kenneth A. (1991), Connors Chemical Kinetics, the study of reaction rates in solution, VCH Publishers. (2nd, ed,) McGraw Hill 75-82

Kim, Y.C., Kim, I., Choi, S. and Rengraj J. Y, (2004). Arsenic removal using mesoporous alumina prepared via a templating method, *Environ Sci. Technol*. (38) 924–931.

Kirk-Othm, (1994) AdsorptionEncyclopedia of Chemical Technology, (1) 582-617.

Komolafe, C.A. Agboola, B.S. Adejumo A.O.D. & Areola J.B. (n.d). Modern conventional water treatment technologies and challenges for optimal utilization in Nigeria.

Koter S, Warszawski A (2000) Electromembrane processes in environment protection. Pol J Environ Stud 9(1):45–56

Lata, S., and Samadder, R. 2014. Removal of heavy metals using rice husk: a review. International Journal of Environmental Research and Development. 4: 165-170.

Margeta K, Logar NZ, S ˇ iljeg M, Farkas A (2013) In: Elshorbagy W (ed) Natural zeolites in water treatment—how effective is their use, water treatment. InTech, Croatia. ISBN 978-953-51-0928-0

Matlock MM, Howerton BS, Atwood DA (2002) Chemical precipitation of heavy metals from acid mine drainage. *Water Res* 36(19):4757–4764

Mikami I, Kitayama R, Okuhara T (2006) Hydrogenations of nitrate and nitrite in water over Pt-promoted Ni catalysts. *ApplCatal A Gen* 297:24–30

Mohamad I Y,Farid N A, Zainal Z A, Azman M. (2008) Charecterization of Rice Husk for Cyclone Gasifier. *J. of app sci*. 8(4) 622-628.

Mohamed, R. M., I. A. Mkhalid and Barakat, M. A. 2015.Rice husk ash as a renewable source for the production of zeolite NaY and its characterization. *Arab J of Chem*. 8(1): 48-53.

Mohammad K. U, Fazul P R. (2017). A study on the potential applications of rice husk derivatives as useful adsorptive material.https://www.researchgate.net/publication/319165720.

Mohana N, Balasubramanian N (2006) In situ electrocatalytic oxidation of acid violet 12 dye effluent. *J Haz Mat* B136:239–243

Morris, M. L. TrippR. &Dankyi,A. A. (2011) "Adoption and Impacts of Improved Corn Production Technology: A Case Study of the Ghana Grains Development Project", Economics Program Mexico, DF, CIMMYT, 1999, pp. 99-100.

Munaf, E., and Zein, R. 2010. The use of rice husk for removal of toxic metals from waste water.*Env. Tech.* 18(3):359-362.

Muntohar, A. S., 2002. Utilization of uncontrolled burnt rice husk ash in soil improvDimensiTeknikSipil. 4(2): 100-105.

Muthadhi, A., Anitha, R. and. Kothandaraman, S. 2007. Rice husk ash properties and its uses: a review. *J of the Inst. of Engs*. 88(5): 50-56.

Nameni, M., AlaviMoghadam, M. R. and Arami M. (2008).Adsorption of hexavalent chromium from aqueous solutionsby wheat bran.Intnl. *J. Environ. Sci. Technol.*,**5,** 161-168.

Nwachcuku N, Gerba CP (2004) Emerging waterborne pathogens: can we kill them all? CurrOpinBiotechnol 15:175–180

Patel, M; Karera, A; P. Prasanna (1987). Effect of thermal and chemical treatment on carbon and silica contents in rice husk. *J. Mater Sci.* 22(7): 2457-2464.

Patil NB; Sharanagouda H (2017). Rice Husk and Its Applications: Review. *Inter. J. Current Microbio. Applied Sci.* 6(10)1144-1156.

Pode, R., (2016). Potential applications of rice husk ash waste from rice husk biomass power plant. Renewable and Sustainable Energy Reviews. 53: 1468-1485.

Prevot AB, Baiocchi C, Brussino MC, Pramauro E, Savarino P, Augugliaro V, Marci G, Palmisano L (2001) Photocatalytic degradation of acid blue 80 in aqueous solution containing TiO2 suspension. *Environ Sci Technol*.35:971

Qu J (2008) Research progress of novel adsorption processes in water purification: a review. *J Environ Sci (China)* 20(1):1–13

Rahman MM, Awang MB, Yusof AM (2012) Preparation, characterization and application of zeolite-Y (Na-Y) for water filtration. *Aus J Basic Appl Sci* 6(1):50–54

Ram NM, Christman RF, Cantor KP (1990) Significance and treatment of volatile organic compounds in water supplies. Lewis Publishers, Chicago

Rameshraja, D; Suresh, S. (2011). Treatment of Tannery Wastewater by Various Oxidation and Combined Processes; *Inter. J. Environ. Resource.* 5(2):349-360.

Rao PV, Gupta N, Bhaskar AS, Jayraj R (2002) Toxins and bioactive compounds from cyanobacteria and their implication on human health. *J Environ Biol* 23(3):215–224

Ringot, D.B., Lerzy, K., Chaplain, J.P., Bonhoure, E. and Larondelle, Y. (2007) In vitro biosorption of ochratoxin A on the yeast industry by-products: comparison of isotherm models, *Bioresour. Technol.* (02)1812–1821.

Rozainee, M., S. P. Ngo, A. A. Salema, K. G. Tan, M. Ariffin and Zainura, Z. N. 2008. Effect of fluidising velocity on the combustion of rice husk in a bench-scale fluidised bed combustor for the production of amorphous rice husk ash. *Biores. Tech*. 99(4): 703-713.

Salmani MH, Abedi M, Mozaffari SA, Sadeghian HA (2017) Modification of pomegranate waste with iron ions a green composite for removal of Pb from aqueous solution: equilibrium, thermodynamic and kinetic studies. AMB Express 7:225. https ://doi.org/10.1186/s1356 8-017-0520-0

SandeepChauhan. Rice husk as a potential adsorbent for removal of metal ions – A review. Pelagia Research Library. Der ChemicaSinica, 2015, 6(6): 90-93.

Sarang, M; Bhattacharyya, S; Behera, RC. (2009). Rice effect of temperature on morphology and phase transformations of nanocrystalline silica obtained from rice husk. Phase transitions: *Multinat J.* 82(5): 377 -386.

Schrank, SG; Jose, HJ; Moreira, RFPM; Schroder, HF. (2004). Comparison of different Advanced Oxidation Process to reduce toxicity and mineralisation of tannery wastewater. *Water Sci Techn,* 50 (5):329-334.

Sivasankar, V., Rajkumar, S; Murugesh, SD. (2012). A Influence of shaking or stirring dynamic methods in the defluoridationbehaviour of activated tamarind fruit shell carbon. *Chem. Eng. J.* 1 (17) 162−172.

Soares OSGP, Orfao JJM, Ruiz-Martinez J, Silvestre-Albero J, Sepu´lveda-Escribano A, Pereira MFR (2010) Pd–Cu/AC and Pt–Cu/AC catalysts for nitrate reduction with hydrogen: influence of calcinations and reduction temperatures. *Chem. Eng. J.* 165:78–88

Strathmann H (2010a) Electrodialysis, a mature technology with a multitude of new applications. Desalination 264:268–288

Strathmann H (2010b) Ion-exchange membrane processes in water treatment. *Sustain Sci Eng* 2(9):141–199

Tadda, M.A., Ahsan A., Shitu A., ElSergany M., Arunkumar T., Bipin Jose, AbdurRazzaque M., NikDaud N.N. (2017). A review on activated carbon: process, application and prospects. *J. Advan Civil Eng Prac. Resear, 2(1):7-13, 2016*

Tiller, K.G. (2004). Heavy metals in soils and their environmental significance. *Adv. Soil Sci*. 9:113–142.

Tzvetkova P, Nickolov R (2012) Modified and unmodified silica gel used for heavy metal ions removal from aqueous solutions. *J Univ Chem Tech Metall* 47(5):498–504

Veil J (2008). Thermal distillation technology for management of produced water and fracflowback water. Water Tech Brief. 2008-1

Vijay D, Bidhan R. (2013). Rice (Oryza sativa L.).https://www.researchgate.net/publication/281152980.

Vijayaraghavan, KTVN. Padmesh, K; Palanivelu, M; Velan, (2006). Biosorption of nickel (II) ions onto Sargassumwightii: application of two-parameter and three parameter isotherm models, *J. Hazard. Mater* (230) 304–308.

Wasse, B; Gezahegn, F; Nestor, F. (2014) 'Removal of Nitrate Ion from Aqueous Solution by Modified Ethiopian Bentonite Clay, Internat.*J. Resear Pharm. Chem.,* 4(1)192-201.

Wehrmann HA, Barcelona MJ, Varljen MD, Blinkiewicz G (1996). Ground-Water Contamination by Volatile Organic Compounds: Site Characterization, Spatial and Temporal Variability ISWS CR-591: Report 591, Prepared for the US Environmental Protection Agency Environmental Monitoring Systems Laboratory Advanced Monitoring Systems Division Aquatic and Subsurface Monitoring Branch.

WHO (2010). International Code of Conduct on the distribution and use of pesticides: guidelines for the registration of pesticides. World Health Organization, Rome.

William B; Jennifer M; Samuel N., (2016). Conversion of Corn Cobs Waste into Activated Carbons for Adsorption of Heavy Metals from Minerals Processing Wastewater. *Inter. J. Environ. Protection Policy* 4(4): 98-103.

Wong YC; Szeto, YS; Cheung, WH; McKay, G. (2004) Adsorption of acid dyes on chitosan-equilibrium isotherm analyses, Process Biochem (53) 693–702.

Xu T (2005) Ion exchange membranes: state of their development and perspective. *J MembrSci* 263:1–29.

Yang RT (1997). Gas separation by adsorption process. Imperial College Press, London Yang RT, Benton DF (2003) Adsorbents: fundamentals and applications,activated carbon, vol Chapter 5. Wiley, Oxford, p 80. doi:10.1002/047144409X.ch5

Yeneneh AM; Maitra S; Eldemerdash U. (2011). Study on biosorption of heavy metals by modified lignocellulosic waste. *J. Appl. Sci.* 11(21)3555-3562.