Kinetic and Isotherm Modelling of adsorption of Cr 3+ metal ions from Tannery wastewater on to unmodified and acid-modified Arabica coffee husks biosorbents

Article · February 2024

DOI: 10.52711/0974-4150.2024.00001

4 authors, including:

Charles Owino Oloo
Dedan Kimathi University of Technology

Gerald K. Muthakia
Dedan Kimathi University of Technology PO

Esther wanja Nthiga
Kenyatta University

ISSN 0974-4169(Print)
0974-4150(Online)
www.ajrconline.org

RESEARCH ARTICLE

Kinetic and Isotherm Modelling of adsorption of Cr^{3+} metal ions from Tannery wastewater on to unmodified and acid-modified Arabica coffee husks biosorbents

Charles Owino Oloo*, Nthiga E. W, Douglas Onyancha, Gerald K. Muthakia
Department of Chemistry, School of Science, Dedan Kimathi University of Technology,
Private Bag, 10143 - Dedan Kimathi, Nyeri-Kenya.
*Corresponding Author E-mail: **owinocharles90@gmail.com**

ABSTRACT:
The kinetics and isotherm modeling of adsorption of Cr^{3+} ions onto unmodified coffee husk (UCH) and acid modified coffee husk (MCH) biosorbent were successfully studied in batch experiments. Equilibrium data were analyzed by Langmuir and Freundlich isotherm models. Equilibrium data best fitted to Langmuir isotherm. The Langmuir adsorption capacity was higher in MCH (6.64 mg/g) compared to the UCH (3.85 mg/g). The adsorption constant, *b*, was less than one in the two adsorption processes suggesting a high affinity of both the UCH and MCH adsorbent for Cr^{3+} ions. The experimental data were fitted well with pseudo second order kinetics with best fitness for both the UCH and MCH with regression coefficient (R^2) of 0.9792 and 0.9956, respectively. The findings revealed that the unmodified and modified coffee husks have potential in removal of Cr^{3+} from tannery wastewater

KEYWORDS: Coffee Husks, Adsorption, Kinetics, Isotherm modeling.

INTRODUCTION:
Tanneries worldwide produce approximately 40 million litres of wastewater that contain chromium every year[1]. Most industries discharge tannery wastewater into sewerage system without proper treatment or in its raw form causing serious environmental impact. There is public concern related to hexavalent compounds owing to their toxic effects on humans, plants, microorganisms and animals. The risks on human health is dependent on the amount, exposure level and duration. Exposure to chromium can damage the skin, eyes, blood, respiratory and immune system[2].

Treatment of tannery wastewater in most tanneries uses physic-chemical methods that include reverse osmosis, precipitation, membrane processes and adsorption[3,12]. Chemical precipitation is the most considered effective technique used to separate heavy metals from industrial waste[4].

Received on 09.06.2023 Modified on 13.09.2023
Accepted on 22.11.2023
Asian J. Research Chem. 2024; 17(1):1-5.
DOI: 10.52711/0974-4150.2024.00001

Most commonly used precipitating agents include: calcium hydroxide, magnesium oxide or calcium magnesium carbonate and sodium hydroxide. Precipitated chromium hydroxide can be easily recycled for tanning process by re-dissolving using an acid.

Adsorption has been universally used in removal of pollutants because of the low cost, low consumption of the chemicals and reagents, ease in handling, as well as ability to recover value added components through desorption and regeneration of adsorbent[5]. The current focus in the field of chemistry primarily revolves around assessing the potential of readily available, sustainable, and cost-effective materials as effective adsorbents to address the pressing issue of heavy metal pollution. This study was initiated in response to this growing trend, and it seeks to adapt Arabica coffee husk as an adsorbent for the removal of Cr^{3+} ions. The uniqueness of this research lies in its approach to adsorbent synthesis and the comprehensive evaluation of adsorption models.

MATERIALS AND METHODS:

Materials:

The chemicals employed in this investigation were of analytical quality, exhibiting a purity exceeding 98.9%. Sodium acetate, sulfuric acid, hydrochloric acid, and chromium chloride hexahydrate were procured from Sigma Aldrich (Kobian, Nairobi). The Arabica coffee husks utilized originated from the coffee farm at Dedan Kimathi University in Kenya.

Adsorbent:

Coffee husk biomass was extensively washed in double-distilled water. After washing and drying the samples were oven-dried at 105°C until there was no longer any weight change, the samples were sieved through a fine sieve. Two sections of the samples were made; one piece underwent acid modification (MCH). The other was labelled "unmodified coffee husk" (UCH) and used in its original form. The chemical alteration was carried out in accordance with Owino *et al.*'s[6,13] method.

Adsorption experiments:

Adsorption experiments were performed in 250mL glass conical flasks at ambient temperature, with agitation provided by a mechanical shaker operating at 120 revolutions per minute. The adsorption parameters that influenced the process (such as pH, the starting concentration of Cr^{3+} ions, the biomass dose, and contact time) had already been determined, Owino *et al.*,[6]. The optimized parameters were, biomass dosage 3g, pH 4.5, metal ion concentration 50mg/L, and time 15min and 25 min for the MCH and UCH, respectively.

Adsorption isotherm and effect of metal ion concentration:

In 100mL Erlenmeyer flasks, batch sorption isotherm studies were conducted. The amount of chromium ions absorbed (qeq) in relation to metal concentration was calculated as follows: For the unmodified and acid-modified coffee husks, 3g of finely ground coffee husks was combined with 10mL of buffer at pH 4.5 and 10mL of chromium (III) solution in the range, 10 - 100mg/L. For two hours, each mixture was stirred. After centrifuging the mixture, the amount of chromium (III) ions (Ceq) in the supernatant solution that was in equilibrium with the coffee husks was calculated using AAS. According to Onyancha et al.[7], the same method was used to determine the concentration in tannery waste.

Adsorption kinetics:

Approximately 3g of coffee husks were combined with 10mL of a 10mg/L Cr(III) solution and 10mL of acetate buffer at pH 4.5 to study the rate of chromium adsorption by both unmodified and acid-modified coffee husks. The mixture was equilibrated in the conical flask. A membrane-equipped syringe was used to draw 2mL of the solution at specified intervals of 10min, and the concentration of chromium was then calculated[6].

Adsorption kinetic models:

The study employed the Pseudo-first-order and Pseudo-second-order adsorption kinetics models, chosen for their convenience in describing solid-solid interactions and the rate of adsorption behaviour. Two kinetic models, pseudo-first order and pseudo-second order, which are depicted in equations (1) and (2), respectively, were chosen to correlate with the experimental data based on their stability towards the solid-liquid adsorption characteristics. The results of the kinetics experiments were analysed to predict the constants of adsorption using these models[8].

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (1)$$

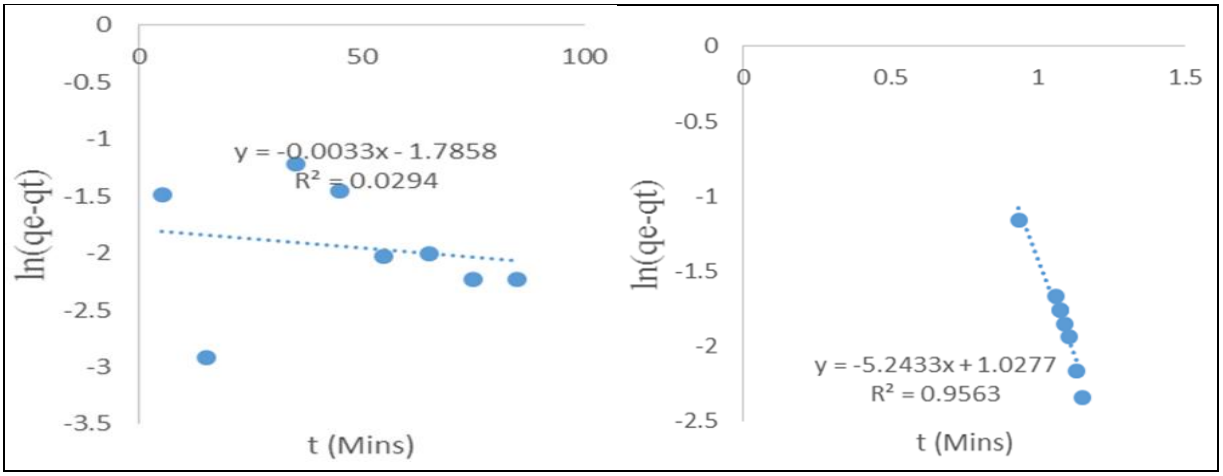
$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

RESULTS AND DISCUSSION:

Adsorption isotherms:

To evaluate the adsorption process and determine the maximum adsorption capacity of the adsorbent, the adsorption data were fitted to the Langmuir and Freundlich equations. The Langmuir equation is based on the assumption that the maximum sorption corresponds to a saturated monolayer of sorbate molecules on the sorbent surface. In order to assess the adsorption process and ascertain the highest adsorption capacity of the adsorbent, the adsorption data were subjected to fitting with the Langmuir and Freundlich equations. The Langmuir equation operates under the premise that the maximum sorption is associated with a saturated monolayer of sorbate molecules on the surface of the sorbent.

Based on the results presented in Figures 1 and 2, it can be concluded that monolayer adsorption is the predominant type of biosorption for metal ions onto both untreated coffee husk (UCH) and acid-modified coffee husk (MCH). The Langmuir isotherm model provides a better fit to the data than the Freundlich isotherm model, as evidenced by the higher regression (R^2) values. Specifically, the R^2 values for UCH and MCH with the Langmuir model were 0.9908 and 0.9912, respectively. In contrast, the R^2 values obtained using the Freundlich isotherm for UCH and MCH were 0.9755 and 0.9777, respectively. However, the lower R^2 values associated with the Freundlich isotherm model indicate that it inadequately describes the relationship between the amount of adsorbed metal ions and their equilibrium concentration in the solution



A B

Fig 1: Langmuir isotherm (a) and Freundlich isotherm (b) plots for adsorption of Cr^{3+} onto UCH

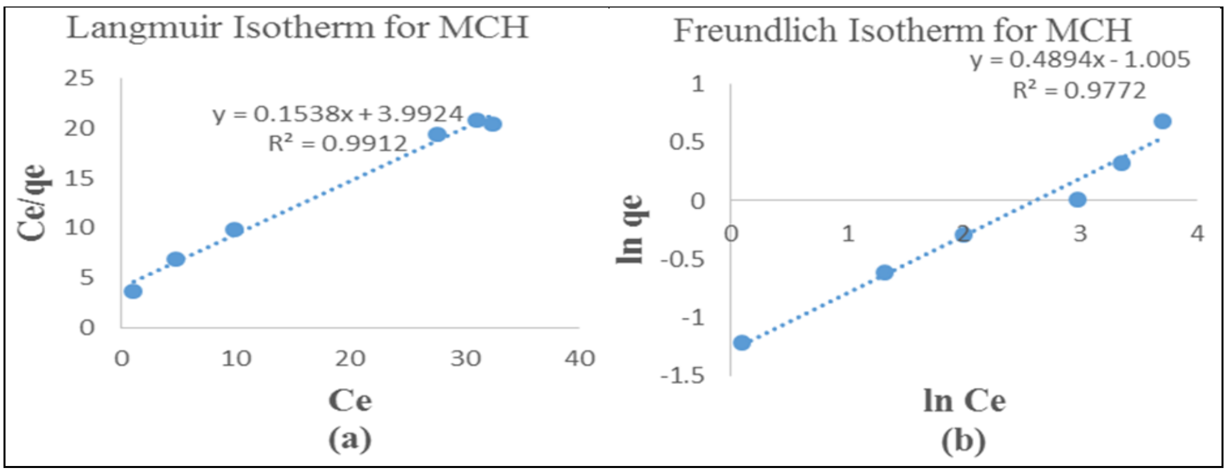


Fig 2: Langmuir isotherm (a) and Freundlich isotherm (b) plots for the adsorption of Cr^{3+} onto modified coffee husk

Freundlich and Langmuir's models were used to analyse the Cr^{3+} ions adsorption capacity by the adsorbents. The findings are illustrated in table 1.

The research results in table 1 show a high correlation between the qe (experimental) and qe (calculated). From the calculated values of R^2 (>0.991), the results fitted well on Langmuir isotherm model (R^2>0.990) as compared to Freundlich isotherm. This means that the adsorption of Cr^{3+} ions on unmodified and modified coffee husk adsorbents can be described by chemisorption and the adsorption is on a monolayer[9,14].

The values of the adsorption capacities qe for the modified adsorbent (6.64mg/g) were higher than those of the unmodified adsorbent (3.85mg/g). The *b* value being less than one in the two adsorption processes suggests a high affinity of both the modified and unmodified adsorbent for Cr^{3+} ions.

Adsorption kinetics:

The adsorption kinetics of Cr^{3+} ions onto UCH and MCH were investigated using two kinetic models, namely the pseudo-first-order and pseudo-second-order models. The findings are reported in table 2:

Table 1: Langmuir and Freundlich constants for Cr^{3+} adsorption on UCH and MCH

Langmuir					Freundlich			
Ads.	qe, exp. (mg/g)	qe, cal (mg/g)	*b* (mg/g)	R^2	K_F (mg/g)	1/n	R^2	Best model
UCH	3.85	3.63	2.18×10^{-2}	0.9908	0.15	0.6146	0.9755	Langmuir
MCH	6.64	6.50	3.85×10^{-2}	0.9912	0.37	0.4894	0.9772	Langmuir

Table 2: Pseudo-first-order and Pseudo-second-order constants for Cr^{3+} using UCH and MCH

Ads.	Pseudo-first-order				Pseudo-second-order			
	qe, exp (mg/g)	qe, cal (mg/g)	k_1 (mg/g/min)	R^2	qe, cal	k_2 (mg/g/min)	R^2	Best model
UCH	0.8898	0.1677	1.7×10^{-2}	0.9016	0.7813	1.05	0.9792	**Pseudo-second order**
MCH	1.2488	2.7946	5.24	0.9563	1.1186	10.6	0.9956	**Pseudo-second order**

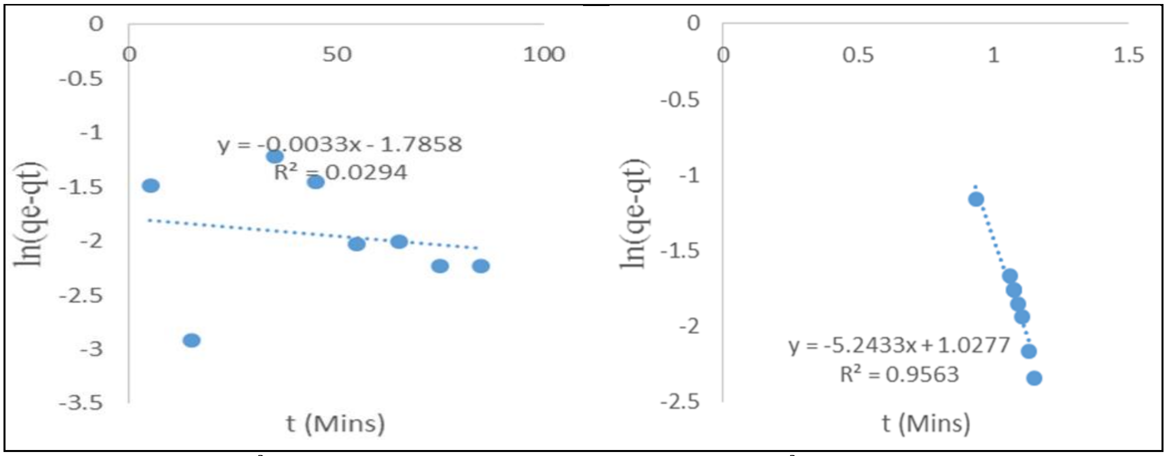


Fig 3. Pseudo 1st order plot of Cr^{3+} ion adsorption onto UCH (A) Pseudo 1st order plot of Cr^{3+} ion adsorption onto MCH (B)

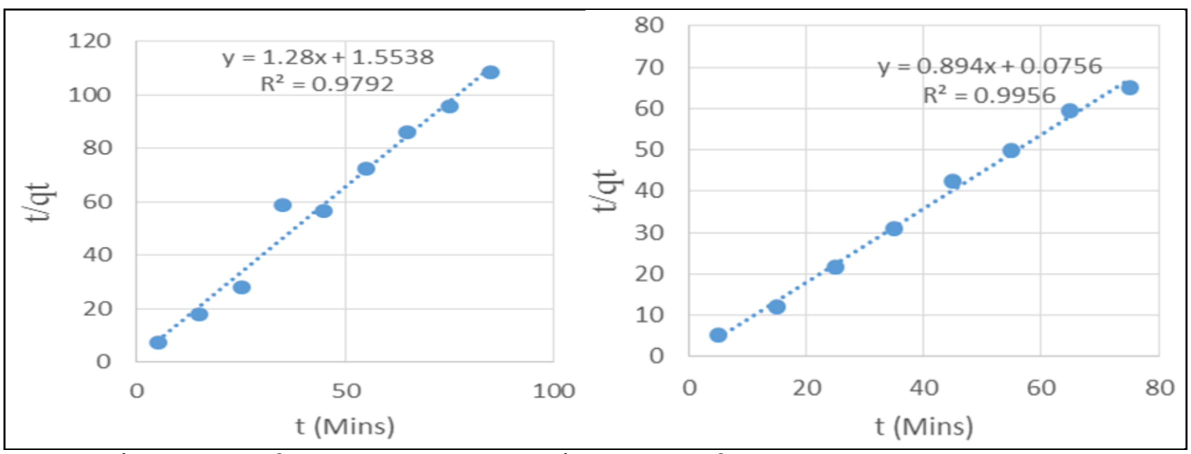


Fig 4: Pseudo 2nd order plot of Cr^{3+} ions onto UCH (A) Pseudo 2nd order plot of Cr^{3+} onto MCH (B)

The results in table 2 show poor R^2 values in the pseudo-first-order kinetics and small calculated q_e values and the experimental q_e values. The adsorption did not fit the pseudo-first-order of kinetics because the values were very far from each other. With an R^2 value greater than 0.9, the pseudo-second-order was a good fit for explaining the kinetics. Furthermore, the experimental and calculated q_e values for Cr^{3+} ions on unmodified and modified adsorbents were nearly identical, implying a chemisorption adsorption mechanism[3] attributed to valence forces through sharing or ion exchange of electrons between the electron-rich surface sites and electron-deficient metal ions[10].

In modified form, the adsorption rate was higher compared to the unmodified one. The modified adsorbent registered a 10.6mg/g/min rate compared to 1.05mg/g/min in the unmodified one. The capacity to adsorb for the value of q_e, cal was lower in the unmodified form than in the modified one. MCH adsorbent showed the greatest value of 1.1186mg/g compared to 0.7813mg/g in the unmodified one. This translates to it that the chromium (III) ions adsorption takes a shorter time to complete the process and also the chemical modification of the material improves the capacity to adsorb. After modifying the coffee husk using sulphuric acid, the surface structure and charge of the adsorbent changed[11].

CONCLUSIONS:

At room temperature and 120 rpm, the adsorption capacity, adsorption isotherm, and kinetic behaviour of unmodified and modified coffee husks in Cr^{3+} adsorption were studied. Compared to the original coffee husk, the modified coffee husk had a greater adsorption capacity. For this study, the selection of adsorption isotherm models included Freundlich and Langmuir, while the kinetic models applied were the pseudo-first order and pseudo-second order. The research data demonstrated that the pseudo-second order adsorption kinetic model provided the best fit, as indicated by its high regression value (R^2).

ACKNOWLEDGMENTS:

Dedan Kimathi University (DeKUT) provided support for this study, which the authors would like to acknowledge. Kenyatta University was also credited for the FT-IR and AAS studies.

REFERENCES:

1. Engy A. Hesham M. A. Amr H. M. Ahr E. Remediation and recycling of chromium from tannery wastewater using combined chemical-biological treatment system. Process Safety and Environmental Protection. 2016; 104: 1–10
2. Zhang, R.; Xiang, Y.; Ran, Q.; Deng, X.; Xiao, Y.; Xiang, L.; Li, Z. Involvement of calcium, Reactive Oxygen species, and ATP in Hexavalent Chromium-Induced Damage in Red Blood Cells. Cell Physiol. Biochem. 2014; 34: 1780–1791
3. Ndung'u S. N; Wanjau R.N; Nthiga E.W; Ndiritu J; Mbugua G.W. Complexation equilibrium studies of Cr2+, Cd2+ and Pb2+ ions onto ethylenediamine quarternised Artocarpus heterophyllus L. seeds from aqueous solution. Journal of Applied Chemistry. 2020; 13(12): 1–12
4. Barakat, M.A. New trends in removing heavy metals from industrial wastewater. Arab. J. Chem. 2011; 4: 361–377
5. Igwe J.C and A.A. Abia. A biosorption process for removing heavy metals from wastewater using biosorbents. Journal of Biotechnology. 2006; 5(12): 167–1179
6. Owino C. O., Nthiga E.W., Gerald K. M. Douglas O. Removal of Cr3+ from tannery wastewater using unmodified and acid-modified Arabica coffee husk adsorbent. 2021; 8(5): 4–9.
7. Onyancha, D; Mavura, W; Ngila, C. J; Ongoma, P; Chacha, J. Studies of chromium removal from tannery wastewaters by algae biosorbents, Spirogyra condensate and Rhizoclonium hieroglyphicum. Journal of Hazardous Materials. 2008; 158(2-3): 605-614.
8. Noor S. N., Hayatu U. S, Muhammad A. A. Z, Norhana M. R, Zulkifli A. M, Shreeshivadasan C. Thanikasalam K, Husna M. Z, Rahmat M. Nabilah Z. Kinetic Equilibrium and Isotherm Modelling Adsorbed Methane Assessment on Synthesized PEEK-Porous Sorbent Carbon of Sustainable Coconut Shell Kernel. Chemical Engineering Transactions. 2019; 72: 247-252 DOI: 10.3303/CET1972042
9. Zhu, H,-X; Cao, X.-J; He, Y.-C; Kong, Q.-P; He, H. and Wang, J. Removal of Cu2+ from aqueous solutions by the novel modified bagasse pulp cellulose: Kinetics, isotherm and mechanism. Journal of Carbohydrate Polymers. 2015; 3(2): 45–60.
10. Kariuki, Z; Kiptoo, J; Onyanja, D. Biosorption studies of lead and copper using Rogers mushroom biomass 'Lepiota hystrix'. South African Journal of Chemical Engineering. 2017; 23: 62–70.
11. Ndug'u S. N, Esther W. N, Ruth N. W, James N. Kinetic Modelling of Cu2+, Cd2+, and Pb2+ ions adsorption onto raw and modified Artocarpus heterophyllus L. seeds from a model solution. Asian Journal of Research in Chemistry. 2021; 14(4): 237–241. DOI: 10.52711/0974-4150.2021.0040.
12. M.N. Thakuria and A.K. Talukdar. Removal of Cu(II) and Cr(III) from drinking water samples by adsorption using rice husk ash. Asian Journal of Research in Chemistry. 2010; 3(3): 626 – 630.
13. Ratna S, Jagdish B, Balaj M. and Milind U. Adsorption of Nickel (II), copper (II) and Iron (III) on Kammoni Leaf Powder: A Case Study. Asian Journal of Research in Chemistry. 2010; 4(1): 100–103
14. Megha R, Sayyed H, Mohd A. A. P. and Mazahar F. Adsorption Studies of Crystal Violet on Sand. Asian Journal of Research in Chemistry. 2011; 4(6): 890–892