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Isothermal Modelling of the Adsorption of Lead (II) Onto Activated Carbon from *Tridax procumbens*

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ABSTRACT

Hypertension and kidney damage have been linked to lead exposure in adults. Any person can be harmed by lead, but pregnant women and their unborn children are especially vulnerable. Presently, lead pollution is removed using membrane separation, ion exchange, precipitation, and biosorption. Biosorption's low operating costs, high efficiency at detoxifying low concentrations of toxicants, and small volume of disposal materials make it the least problematic of these technologies. The biosorption of lead (II) onto activated carbon from *Tridax procumbens* is remodeled using nonlinear regression and the optimal mode was determined by a series of error function assessments. The Freundlich model performed best in statistical tests including root-mean-square error (RMSE), adjusted coefficient of determination ($\text{adj}R^2$), bias factor (BF), accuracy factor (AF), and corrected Akaike Information Criterion (AICc). The calculated Freundlich parameters k_F value using nonlinear regression was 1.334 (1/g) (95% confidence interval from 0.821 to 1.847) and n_F value of 3.872 (95% C.I. from 1.972 to 5.771). Modelling using a nonlinear approach allows for the calculation of uncertainty range in terms of 95% confidence interval that would be useful for model comparison and discriminant in future studies

INTRODUCTION

Heavy metals are increasingly being released into the environment as a byproduct of mining, electroplating, alloy preparation, pulp-paper, and fertilizer production, among other industrial processes. The issue of pollution involving heavy metals is of paramount importance due to the accumulation of heavy metals in the food chain and the severe health concerns they cause to living beings. Lead is a naturally occurring toxic element found in the Earth's crust. Polluting large areas, exposing large numbers of people, and negatively impacting public health are all direct results of its widespread use in a variety of countries. More than 75% of all lead is used in the production of lead-acid car batteries. But lead is also used in many other products, such as pigments, paints, solder, stained glass, lead crystal glassware, ammunition, ceramic glazes, jewelry, toys, cosmetics, and traditional medicines. If the water pipes themselves are made of

lead or if the pipes are joined together with lead-based solder, then the water you drink may contain lead. The majority of lead in international trade today is derived from recycled materials. Lead's negative effects on children are more severe because their developing brains and nervous systems are more susceptible to its toxicity. Adults who are exposed to high levels of lead are more likely to develop hypertension and kidney damage. Lead exposure is dangerous for everyone, but it can have devastating effects on pregnant women and their babies [1–3]. Anemia, hepatitis, encephalopathy, and nephritic syndrome have all been linked to lead levels in drinking water that are above the legal limit of 0.05 mg/L. Due to its high biosorption capacity and selectivity, low cost, and low environmental risk, biosorption is a promising approach for the removal of heavy metals from wastewater [1–3].

It is critical to correctly assign the kinetics and isotherms of biosorption in order to comprehend the biosorption process of toxicants. Estimating uncertainty of the parameters of the kinetics, which are often displayed as a 95 percent confidence interval range, can be made more challenging by the linearization of a clearly nonlinear curve, which can cause problems on the error structure of the data [4]. Error in the independent variable might also be introduced during data transformation for linearization. In addition, the fitted parameter values for the linear and nonlinear variants of the model can differ due to changes in the weight placed on each data point [5]. In this study the published data from the biosorption of lead (II) onto activated carbon from *Tridax procumbens* [6] is remodeled using nonlinear regression of several isothermal models (**Table 1**) and the optimal mode was determined by a series of error function assessments. Given that the isotherms in the paper were proposed using a linearized modeling version, this modeling analysis was warranted.

Table 1. Isotherm models utilized in this study.

Model	Formula	Ref
Henry's law	$q_e = HC_e$	[7]
Langmuir isotherm	$q_e = \frac{q_{mL}b_L C_e}{1 + b_L C_e}$	[8]
Freundlich isotherm	$q_e = K_F C_e^{\frac{1}{n_F}}$	[9]
Sips isotherm	$q_e = \frac{K_s q_{ms} C_e^{\frac{1}{n_s}}}{1 + K_s C_e^{\frac{1}{n_s}}}$	[10]
Toth isotherm	$q_e = \frac{q_{mT} C_e}{(K_T + C_e^{\frac{1}{n_T}})^{n_T}}$	[11]
BET isotherm	$q_e = \frac{q_{mBET} \alpha_{BET} C_e}{(1 - \beta_{BET} C_e)(1 - \beta_{BET} C_e + \alpha_{BET} C_e)}$	[12]
Baudu isotherm	$q_e = \frac{q_{mB} b_B C_e^{(1+x+y)}}{1 + b_B C_e^{(1+x+y)}}$	[13]
Fritz-Schlunder-IV isotherm	$q_e = \frac{A_{FS} C_e^{\alpha_{FS}}}{1 + B_{FS} C_e^{\beta_{FS}}}$	[14]
Fritz-Schlunder-V isotherm	$q_e = \frac{q_{mFS} K_1 C_e^{\alpha_{FS}}}{1 + K_2 C_e^{\beta_{FS}}}$	[14]

METHODS

Data acquisition and fitting

Data from Figure 5a from a published work [6] were digitized using the software Webplotdigitizer 2.5 [15]. The accuracy of data digitized with this program has been verified [16,17]. The data were first converted to q_t values and then nonlinearly regressed using the curve-fitting software CurveExpert Professional software (Version 1.6).

Statistical analysis

Commonly used statistical discriminatory methods such as corrected AICc (Akaike Information Criterion), Bayesian Information Criterion (BIC), Hannan and Quinn's Criterion (HQ), Root-Mean-Square Error (RMSE), bias factor (BF), accuracy factor (AF) and adjusted coefficient of determination (R^2).

The RMSE was calculated according to **Eq. (1)**, [4], and smaller number of parameters is expected to give a smaller RMSE values. n is the number of experimental data, Ob_i and Pd_i are the

experimental and predicted data while p is the number of parameters.

$$RMSE = \sqrt{\frac{\sum_{i=1}^n (Pd_i - Ob_i)^2}{n - p}} \quad (\text{Eqn. 1})$$

As R^2 or the coefficient of determination ignores the number of parameters in a model, the adjusted R^2 is utilized to overcome this issue. In the equation (**Eqns. 2 and 3**), the total variance of the y-variable is denoted by S_y^2 while RMS is the Residual Mean Square.

$$Adjusted (R^2) = 1 - \frac{RMS}{S_y^2} \quad (\text{Eqn. 2})$$

$$Adjusted (R^2) = 1 - \frac{(1 - R^2)(n - 1)}{(n - p - 1)} \quad (\text{Eqn. 3})$$

The Akaike Information Criterion (AIC) is based on the information theory. It balances between the goodness of fit of a particular model and the complexity of a model [18]. To handle data having a high number of parameters or a smaller number of values corrected Akaike information criterion (AICc) is utilized [19]. The AICc is calculated as follows (**Eqn. 4**), where p signifies the quantity of parameters and n signify the quantity of data points. A model with a smaller value of AICc is deemed likely more correct [19].

$$AICc = 2p + n \ln \left(\frac{RSS}{n} \right) + 2(p+1) \frac{(p+2)}{n-p-2} \quad (\text{Eqn. 4})$$

Aside from AICc, Bayesian Information Criterion (BIC) (**Eqn. 5**) is another statistical method that is based on information theory. This error function penalizes the number of parameters more strongly than AIC [20].

$$BIC = n \ln \frac{RSS}{n} + k \ln (n) \quad (\text{Eqn. 5})$$

A further error function method based on the information theory is the Hannan–Quinn information criterion (HQC) (**Eqn. 6**). The HQC is strongly consistent unlike AIC due to the $\ln \ln n$ term in the equation [19];

$$HQC = n \ln \frac{RSS}{n} + 2 \times k \times \ln(\ln n) \quad (\text{Eqn. 6})$$

Further error function analysis that originates from the work of Ross [21] are the Accuracy Factor (AF) and Bias Factor (BF). These error functions test the statistical evaluation of models for the goodness-of-fit but do not penalize for number of parameter (**Eqns. 7 and 8**).

$$\text{Bias factor} = 10^{\left(\sum_{i=1}^n \log \frac{(Pd_i / Ob_i)}{n} \right)} \quad (\text{Eqn. 7})$$

$$\text{Accuracy factor} = 10^{\left(\sum_{i=1}^n \log \frac{(Pd_i / Ob_i)}{n} \right)} \quad (\text{Eqn. 8})$$

RESULTS AND DISCUSSION

The equilibrium data from [6] was analyzed using nine models—Henry, Langmuir, Freundlich, BET, Toth, Sips, Fritz-Schlunder IV, Baudu and Fritz-Schlunder V, and fitted using non-linear

regression (Figs. 1-9). The Freundlich model performed best in statistical tests including root-mean-square error (RMSE), adjusted coefficient of determination ($\text{adj}R^2$), bias factor (BF), accuracy factor (AF), and corrected Akaike Information Criterion (AICc) (Table 2). This is the same to the published work [6] using a linearized form where the Freundlich models best represent the biosorption and the maximum biosorption capacity for the model k_F (Freundlich isotherm constant) is 1.2511 1/g and n_F or the Freundlich exponent value of 3.53. The calculated Freundlich parameters k_F value using nonlinear regression was 1.334 (1/g) (95% confidence interval from 0.821 to 1.847) and n_F value of 3.872 (95% C.I. from 1.972 to 5.771).

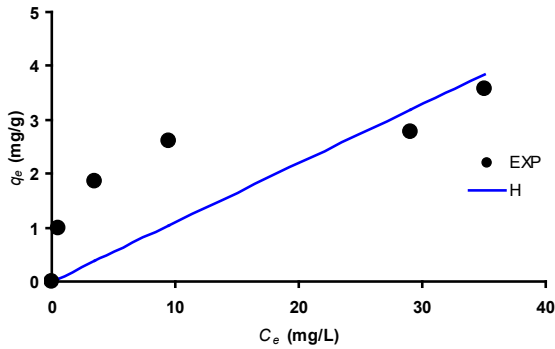


Fig. 1. Isotherm of biosorption of lead (II) onto activated carbon from *Tridax procumbens* as modelled using the Henry model.

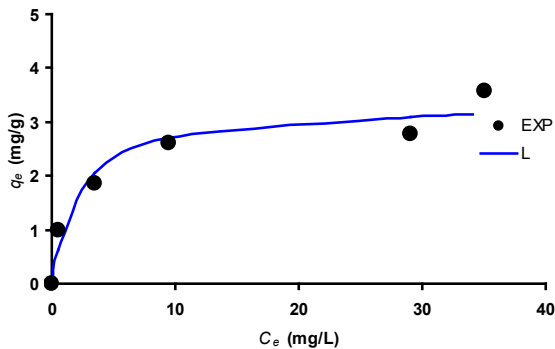


Fig. 2. Isotherm of biosorption of lead (II) onto activated carbon from *Tridax procumbens* as modelled using the Langmuir model.

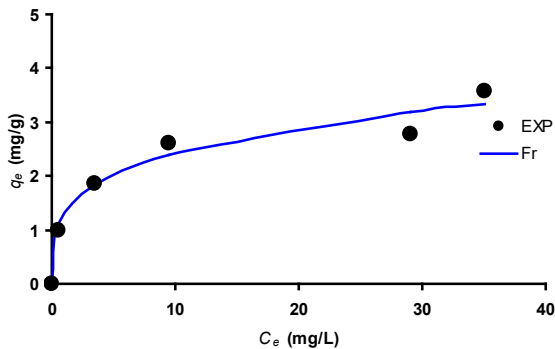


Fig. 3. Isotherm of biosorption of lead (II) onto activated carbon from *Tridax procumbens* as modelled using the Freundlich model.

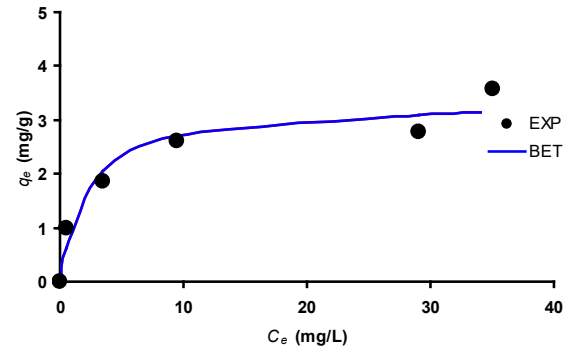


Fig. 4. Isotherm of biosorption of lead (II) onto activated carbon from *Tridax procumbens* as modelled using the BET model.

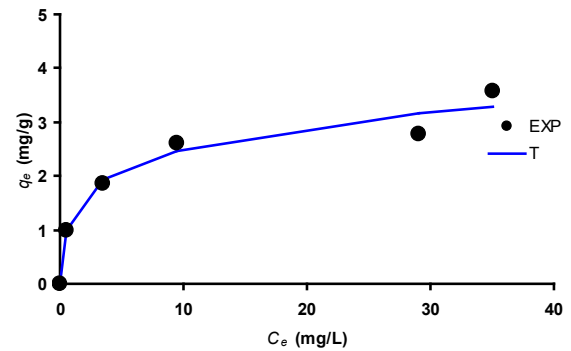


Fig. 5. Isotherm of biosorption of lead (II) onto activated carbon from *Tridax procumbens* as modelled using the Toth model.

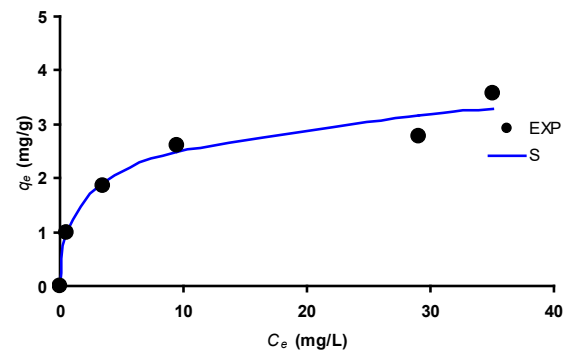


Fig. 6. Isotherm of biosorption of lead (II) onto activated carbon from *Tridax procumbens* as modelled using the Sips model.

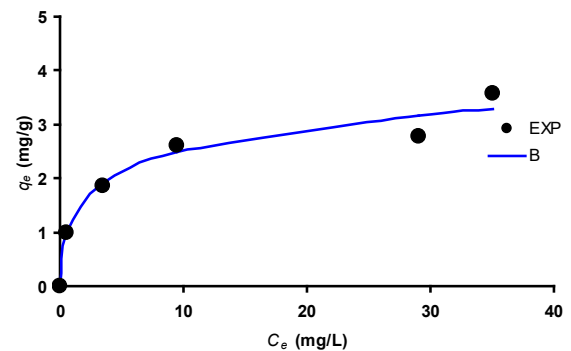


Fig. 7. Isotherm of biosorption of lead (II) onto activated carbon from *Tridax procumbens* as modelled using the Baudu model.

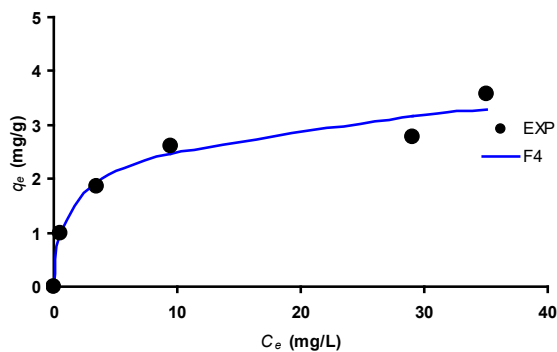


Fig. 8. Isotherm of biosorption of lead (II) onto activated carbon from *Tridax procumbens* as modelled using the Fritz-Schlunder-IV model.

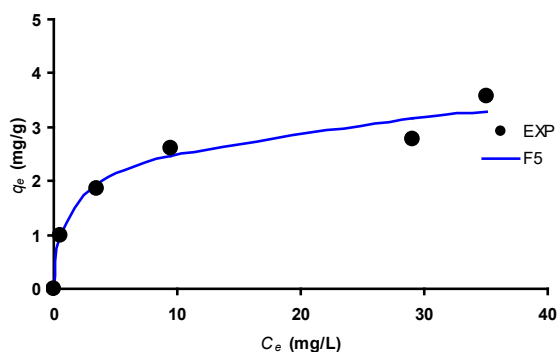


Fig. 9. Isotherm of biosorption of lead (II) onto activated carbon from *Tridax procumbens* as modelled using the Fritz-Schlunder-V model.

Table 2. Error function analysis for the fitting of the isotherms of lead (II) onto activated carbon from *Tridax procumbens*.

Model	<i>p</i>	RMSE	adR ²	AICc	BIC	HQC	BF	AF
Henry	1	1.08	0.49	9.79	1.58	0.96	0.42	2.54
Langmuir	2	0.35	0.91	6.81	-11.61	-12.86	0.94	1.15
Freundlich	2	0.27	0.94	3.79	-14.62	-15.87	1.01	1.07
BET	3	0.40	0.87	38.81	-9.82	-11.69	0.94	1.15
Toth	3	0.29	0.92	35.03	-13.59	-15.47	1.00	1.05
Sips	3	0.29	0.92	35.13	-13.50	-15.38	1.00	1.05
Baudu	4	0.36	0.84	n.a.	-11.72	-14.22	1.00	1.05
F4	4	0.36	0.85	n.a.	-11.80	-14.30	1.00	1.05
F5	5	0.50	n.a.	n.a.	-10.01	-13.14	1.00	1.05

Note:
 RMSE Root mean Square Error
p no of parameters
 adR² Adjusted Coefficient of determination
 BF Bias factor
 AF Accuracy factor
 AICc Adjusted Akaike Information Criterion
 BIC Bayesian Information Criterion
 HQC Hannan–Quinn information criterion
 n.a. Not available

In a Freundlich adsorption isotherm, the adsorbate forms a monomolecular layer on the adsorbent's surface. The Freundlich equation, originally developed to describe adsorption and desorption in the gas phase, is a popular empirical adsorption model. The Freundlich equation is valid up to a certain concentration after which it becomes nonlinear, and while it does provide important information about sorption of particles, it is purely empirical [9,22,23]. The reversible and non-ideal adsorption process is described by the Freundlich adsorption isotherm model. The Freundlich model, in contrast to the Langmuir isotherm model, can be applied to multilayer adsorption. Because of this isotherm model, the adsorption heat and affinities can be unevenly distributed across a heterogeneous

surface. The exponential distribution of active sites and their energies, as well as the heterogeneity of the surface, are all defined by the expression of the Freundlich isotherm model. The Freundlich isotherm adsorption model was first created for the adsorption of animal charcoal. This experiment proved that the mass ratio of the adsorbate onto a fixed adsorbent changed depending on the solution concentration. What this means is that the adsorbed amount is the total amount of adsorption at all of the sites. After the more stable binding sites are taken up first, the adsorption energy drops off exponentially [24–26]. The Freundlich model was also the best model for lead(II) sorption by a modified Jordanian zeolite [27], by a Guar gum/bentonite bionanocomposite [28], *Chlorococcum aquaticum* biomass [29] and nanoparticle adsorbents of cellulose origin [30] and the sorption of other metal and radionuclides [31–36].

CONCLUSION

Finally, the biosorption isotherm data for lead (II) onto activated carbon from *Tridax procumbens* was successfully analyzed using a variety of models with one to five parameters, including the Henry, BET, Langmuir, Freundlich, Toth, Baudu, Sips, Fritz-Schlunder IV, and Fritz-Schlunder V models. The Freundlich model performed best in statistical tests including root-mean-square error (RMSE), adjusted coefficient of determination (adjR²), bias factor (BF), accuracy factor (AF), and corrected Akaike Information Criterion (AICc). The calculated Freundlich parameters *k_F* value using nonlinear regression was 1.334 (1/g) (95% confidence interval from 0.821 to 1.847) and *n_F* value of 3.872 (95% C.I. from 1.972 to 5.771). Nonlinear modeling enables the determination of a 95 percent confidence interval for the uncertainty range, which can be used in model comparison and discriminant analysis.

REFERENCES

1. Raviraja A, Vishal Babu GN, Sehgal A, Saper RB, Jayawardene I, Amarasinghwardena CJ, et al. Three cases of lead toxicity associated with consumption of ayurvedic medicines. *Indian J Clin Biochem.* 2010;25(3):326–9.
2. Alissa EM, Ferns GA. Heavy metal poisoning and cardiovascular disease. *J Toxicol.* 2011;2011:870125.
3. Nepalia A, Singh A, Mathur N, Pareek S. Toxicity assessment of popular baby skin care products from Indian market using microbial bioassays and chemical methods. *Int J Environ Sci Technol.* 2018 Nov 1;15(11):2317–24.
4. Motulsky HJ, Ransnas LA. Fitting curves to data using nonlinear regression: a practical and nonmathematical review. *FASEB J Off Publ Fed Am Soc Exp Biol.* 1987;1(5):365–74.
5. Tran HN, You SJ, Hosseini-Bandegharai A, Chao HP. Mistakes and inconsistencies regarding adsorption of contaminants from aqueous solutions: A critical review. *Water Res.* 2017 Sep 1;120:88–116.
6. Malairajan S. Removal of lead(II) and cadmium(II) ions from wastewater using activated biocarbon. *scienceasia.* 2011 Jun 1;37(1):115–9.
7. Ridha FN, Webley PA. Anomalous Henry's law behavior of nitrogen and carbon dioxide adsorption on alkali-exchanged chabazite zeolites. *Sep Purif Technol.* 2009;67(3):336–43.
8. Langmuir I. The adsorption of gases on plane surfaces of glass, mica and platinum. *J Am Chem Soc.* 1918;40(9):1361–403.
9. Freundlich H. Over the adsorption in solution. *Z Für Phys Chem.* 1906;57:385–470.
10. Sips R. On the structure of a catalyst surface. *J Chem Phys.* 1948;16(5):490–5.
11. Toth J. State equations of the solid-gas interface layers. *Acta Chim Acad Sci Hung.* 1971;69(3):311–28.
12. Brunauer S, Emmett PH, Teller E. Adsorption of gases in multimolecular layers. *J Am Chem Soc.* 1938;60(2):309–19.
13. Baudu M. Etude des interactions solute-fibres de charbon actif. Application et regeneration. Université de Rennes I; 1990.

14. Fritz W, Schluender EU. Simultaneous adsorption equilibria of organic solutes in dilute aqueous solutions on activated carbon. *Chem Eng Sci.* 1974;29(5):1279–82.
15. Rohatgi A. WebPlotDigitizer. <http://arohatgi.info/WebPlotDigitizer/app/> Accessed June 2 2014.; 2015.
16. Halmi MIE, Shukor MS, Johari WLW, Shukor MY. Mathematical modelling of the degradation kinetics of *Bacillus cereus* grown on phenol. *J Environ Bioremediation Toxicol.* 2014;2(1):1–5.
17. Khare KS, Phelan Jr FR. Quantitative comparison of atomistic simulations with experiment for a cross-linked epoxy: A specific volume-cooling rate analysis. *Macromolecules.* 2018;51(2):564–75.
18. Akaike H. New look at the statistical model identification. *IEEE Trans Autom Control.* 1974;AC-19(6):716–23.
19. Burnham KP, Anderson DR. Model Selection and Multimodel Inference: A Practical Information-Theoretic Approach. Springer Science & Business Media; 2002. 528 p.
20. Kass RE, Raftery AE. Bayes Factors. *J Am Stat Assoc.* 1995 Jun 1;90(430):773–95.
21. Ross T, McMeekin TA. Predictive microbiology. *Int J Food Microbiol.* 1994;23(3–4):241–64.
22. Barkhordar B, Ghias Aldin M. Comparison of Langmuir and Freundlich equilibria in Cr, Cu and Ni adsorption by Sargassum. *Iran J Environ Health Sci Eng.* 2004 Jan 1;1(2):58–64.
23. Crittenden JC, Watson HM. Adsorption. In: *MWH's Water Treatment: Principles and Design, Third Edition* [Internet]. John Wiley & Sons, Ltd; 2012 [cited 2020 May 31]. p. 1117–262. Available from: <https://onlinelibrary.wiley.com/doi/abs/10.1002/9781118131473.ch15>
24. Foo KY, Hameed BH. Insights into the modeling of adsorption isotherm systems. *Chem Eng J.* 2010;156(1):2–10.
25. Al-Ghouti MA, Da'ana DA. Guidelines for the use and interpretation of adsorption isotherm models: A review. *J Hazard Mater.* 2020 Jul 5;393:122383.
26. Hu Q, Pang S, Wang D. In-depth Insights into Mathematical Characteristics, Selection Criteria and Common Mistakes of Adsorption Kinetic Models: A Critical Review. *Sep Purif Rev.* 2021 Jul 1;0(0):1–19.
27. Baker H. Removal of Lead Ions from Waste Water Using Modified Jordanian Zeolite. *Chem Sci Int J.* 2020 Nov 9;19–30.
28. Ahmad R, Mirza A. Synthesis of Guar gum/bentonite a novel bionanocomposite: Isotherms, kinetics and thermodynamic studies for the removal of Pb (II) and crystal violet dye. *J Mol Liq.* 2018 Jan 1;249:805–14.
29. Liyanage LMM, Lakmali WGM, Athukorala SNP, Jayasundera KB. Application of live *Chlorococcum aquaticum* biomass for the removal of Pb(II) from aqueous solutions. *J Appl Phycol.* 2020 Dec 1;32(6):4069–80.
30. Yakubu A, Olatunji GA, Adekola FA. Modified/Unmodified Nanoparticle Adsorbents of Cellulose Origin With High Adsorptive Potential for Removal of Pb(II) From Aqueous Solution. *Eur Sci J ESJ.* 2017 Sep 30;13(27):425–425.
31. Daifullah A a. M, Moloukhia H. Removal of cobalt and europium radioisotopes using activated carbon prepared from apricot stones. *Isot Radiat Res* [Internet]. 2002 Jul 1 [cited 2022 Jul 26];34. Available from: <https://www.osti.gov/etdeweb/biblio/20395653>
32. Moloukhia H, El-Zakla T, Belacy N. Use of lignocellulosic biomass in removal of ⁶⁰Co and ¹³⁷Cs from radioactive wastewater. *Arab J Nucl Sci Appl.* 2010;43(1):121–30.
33. Rajapaksha AU, Vithanage M, Jayarathna L, Kumara CK. Natural Red Earth as a low cost material for arsenic removal: Kinetics and the effect of competing ions. *Appl Geochem.* 2011 Apr 1;26(4):648–54.
34. Mahapatra A, Mishra BG, Hota G. Electrospun Fe₂O₃–Al₂O₃ nanocomposite fibers as efficient adsorbent for removal of heavy metal ions from aqueous solution. *J Hazard Mater.* 2013 Aug 15;258–259:116–23.
35. Sharifi S, Nabizadeh R, Akbarpour B, Azari A, Ghaffari HR, Nazmara S, et al. Modeling and optimizing parameters affecting hexavalent chromium adsorption from aqueous solutions using Ti-XAD7 nanocomposite: RSM-CCD approach, kinetic, and isotherm studies. *J Environ Health Sci Eng.* 2019 Dec 1;17(2):873–88.
36. Calderón C, Levio-Raimán M, Díez MC. Cadmium removal for marine food application: comparative study of different adsorbents. *Int J Environ Sci Technol* [Internet]. 2021 Oct 29 [cited 2022 Jul 26]; Available from: <https://doi.org/10.1007/s13762-021-03746-9>