Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.journals.elsevier.com/journal-of-the-taiwan-institute-of-chemical-engineers

Process development of guava leaves with alkali in removal of zinc ions from synthetic wastewater

Chanda Sireesha [a], Kaliannan Durairaj [b,*], Balamuralikrishnan Balasubramanian [c], Shanmugam Sumithra [a,*], Rajendran Subha [d], Hesam Kamyab [e,f,*], Shreeshivadasan Chelliapan [g,*]

[a] *Department of Environmental Science, Yogi Vemana University, Vemanapuram, Andhra Pradesh 516005, India*
[b] *Zoonosis Research Center, Department of Infection Biology, School of Medicine, Wonkwang University, Iksan 54538, South Korea*
[c] *Department of Food Science and Biotechnology, College of Life Science, Sejong University, Seoul 05006, South Korea*
[d] *Department of Chemistry, Cauvery College for Women, Trichy, Tamil Nadu 620018, India*
[e] *Faculty of Architecture and Urbanism, UTE University, Calle Rumipamba S/N and Bourgeois, Quito, Ecuador*
[f] *Process Systems Engineering Centre, Department of Chemical and Energy Engineering, Universiti Teknologi Malaysia, Skudai, Johor, Malaysia*
[g] *Engineering Department, Razak Faculty of Technology and Informatics, Universiti Teknologi Malaysia, Jln Sultan Yahya Petra, Kuala Lumpur 54100, Malaysia*

ARTICLE INFO

Keywords:
Zinc ion removal
KOH treated guava leaves
Langmuir
Adsorption
Wastewater treatment

ABSTRACT

Background: This research investigation delves into the efficient removal of zinc ions from synthetic wastewater through the utilization of KOH treated guava leaves as an adsorbent. The study employs advanced analytical techniques including SEM, FTIR, XRD, and BET analysis to characterize the physicochemical properties of the treated guava leaves. The research extensively explores the impact of various experimental factors on the adsorption process, encompassing agitation time, adsorbent dosage, pH levels, and desorption, to identify optimal conditions for maximum Zn (II) ion removal.

Methods: The research methodology involves subjecting guava leaves treated with KOH to thorough analysis using SEM, FTIR, XRD, and BET techniques to gain insights into their physical and chemical attributes. The study systematically investigates the adsorption process by manipulating crucial parameters such as agitation time, adsorbent dosage, and pH levels. Different isotherm models including Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich are applied to comprehend the adsorption mechanism. Additionally, kinetic calculations are performed, leading to the determination that the pseudo-second-order model best fits the removal of zinc metal.

Significant Findings: The research uncovers essential findings regarding the efficacy of KOH treated guava leaves as an adsorbent for zinc ions. Optimum conditions are pH 3 are identified, an adsorbent dosage of 100 mg/L, and an equilibrium period of 20 min, resulting in peak efficiency of the adsorption process. The study reveals an adsorption capacity of 14.5 mg/g for the studied metal, emphasizing the potential of KOH treated guava leaves as an efficient adsorbent for zinc ions. The adsorption capacity is 5.1 mg/g for the untreated guava leaves. The findings underscore the feasibility of utilizing this eco-friendly approach for wastewater management, thereby contributing to environmental remediation and pollution control efforts. The research highlights the practical application of KOH treated guava leaves in wastewater treatment processes, advocating for further exploration and optimization of this sustainable solution to address heavy metal contamination and promote greener technologies for water purification and waste management.

1. Introduction

Contaminations of heavy metals in water are a global problem to the environment due to their accumulation through the food chain and their toxic effects [1]. Metal ions can be present in water through natural processes or as a result of human activities, including the leaching of ore

---

* Corresponding authors.
E-mail addresses: kmdurairaj@gmail.com (K. Durairaj), ssumithra1@yahoo.co.in (S. Sumithra), khesam2@live.utm.my, hesam_kamayb@yahoo.com (H. Kamyab), shreeshivadasan.kl@utm.my (S. Chelliapan).

https://doi.org/10.1016/j.jtice.2023.105283
Received 21 August 2023; Received in revised form 19 November 2023; Accepted 4 December 2023

Please cite this article as: Chanda Sireesha et al., *Journal of the Taiwan Institute of Chemical Engineers*, https://doi.org/10.1016/j.jtice.2023.105283

deposits and the release of industrial effluents and solid waste [2]. Industries such as automobiles, the production of protective coatings, cosmetic industry, battery manufacturing, rubbers, fertilizers, mining, ointments, antiseptics, paints, varnishes etc. are more responsible for zinc pollution [3,4]. Among the potentially hazardous metals, zinc has been frequently identified as a predominant metal ion in rainfall [5,6]. The World Health Organization (WHO) have categorized 13 heavy metals as toxic, and among them zinc [7]. In a study by Atangana [8], it was highlighted that elevated levels of zinc chloride can lead to adverse health effects in humans, including symptoms like dizziness, muscle weakness, stomach pain, and kidney disease. Given these concerns, the development of efficient technologies to address zinc contamination becomes imperative. Regulatory authorities have established stringent guidelines for the acceptable levels of toxic heavy metals discharge into water bodies. The WHO has defined a permissible limit of 3 mg/L for zinc concentration in drinking water [9].

S. No	Metal	Health Effects
1.	Zinc	Causes short-term illness, metal fume fever, restlessness, skin irritations, nausea and anemia.

There are different treatment methods for the removal of heavy metals, such as ion –exchange, chemical and physical precipitation, coagulation, flotation, and electrochemical remediation [10]. Many methods are characterized by incomplete removal of pollutants, low selectivity, high operational costs and the production of large amounts of residues [11]. Over the past few years, adsorption has been preferred by many researchers due to its inexpressive cost and high efficiency. So, there is a need to develop adsorbent materials featuring high feasibility and availability, low costs and high adsorption capacity are required. Recently some of the materials tested for the removal of zinc are chemically modified biosorbents [12], banana stalk biochar [13], tea waste [14], *Boodlea struveiodes* [3], saw dust [15], alginate-immobilized *Penicillium* species [16], groundnut husk ash [17] etc. The primary objective of this study was (i) To evaluate the adsorption efficiency of guava leaves, an agricultural waste, for eliminating zinc ions from aqueous solutions; (ii) To investigate several factors, including the initial pH of the zinc-containing water; (iii) To explore the impact of the quantity of adsorbent used, and the initial metal concentrations, along with their respective contact times or agitation times.

2. Materials and methods

2.1. Sample collection and adsorbent preparation

Guava leaves were collected from the Yogi Vemana University campus. The leaves were cleaned with distilled water. The cleaned leaves were dried at 90 °C for 4 h in a hot air oven. The dried leaves were mixed in a food processing blender. The powder was then sieved to obtain a particle size of 100 μm (100 - 250 μm) and used as an adsorbent. About fifty grams of the adsorbent powder were placed in contact with 500 mL of a potassium hydroxide solution with a concentration of 0.15 mol/dm^3 and stirred overnight. Subsequently, the resulting powder was rinsed with distilled water, and this procedure was iterated two or more times to ensure the thorough removal of KOH. The remaining residue was then dried overnight at 90 °C for further processing [18].

2.2. Characterization of adsorbent

The adsorbent's crystal structure and phase formation were analyzed through X-ray diffraction using a Rigaku X-ray diffractometer (XRD, Miniflex 600, Japan). The predominant functional groups within the adsorbent were estimated using Fourier-transform infrared spectrophotometry on a Perkin-Elmer spectrometer (FTIR, Bruker Alpha II, USA). Surface morphology and area were assessed via scanning electron microscopy (SEM, JSM IT 500, JEOL, Japan) and Brunauer-Emmett-Teller (Quantachrome, USA) analysis.

2.3. Zinc solution preparation

The standard zinc solution was prepared from $ZnSO_4$. $7H_2O$ in 1 L volumetric flask to obtain a solution of 1000 mg/L. The above solutions were again diluted in deionised water to get a concentration of 5, 10, 20, 30 and 40 mg/L, respectively. The pH of each solution was adjusted to 6 using either 0.1 M HCl or 0.1 M NaOH, as per the requirement, in conjunction with the chosen adsorbent.

2.4. Experiment

Batch mode adsorption experiment was conducted to investigate the impact of the parameters like zinc ion concentration, contact/agitation time, dosage of adsorbent, pH and desorption. After the prescribed time study, the solution was filtered and examined using AAS (Shimadzu, Model no. AA-6880) at 213.9 nm with a slit width of 1 nm.

The capacity of adsorption at equilibrium time and the removal percentage for zinc ions were set by:

$$\mathrm{R\%} = \frac{\mathrm{C_i} - \mathrm{C_e}}{\mathrm{C_i}} \times 100 \tag{1}$$

$$q_e = \frac{C_i - C_e}{w} \times V \tag{2}$$

Here, Ci represents the initial concentration of the adsorbate (mg/L), Ce represents the equilibrium concentration of the adsorbate (mg/L), V represents the volume of the metal solution (L), and 'w' represents the mass of the adsorbent (g).

3. Results and discussion

3.1. Characteristics of adsorbent

Through an assessment of composite material development, meticulously examined the impact of pH, adsorbent dosage, zinc ion concentration, contact time, and temperature on the uptake, leading to enhanced and optimized values. The resulting modified guava leaves composite material exhibited superior efficiency compared to previously reported materials. The surface area of the composite material was assessed via BET analysis utilizing N_2 gas, revealing a surface area of m^2/g alongside micropore volume. A comparable study by Polladi et al. [19] demonstrated a surface area of 31.8 m^2/g for chitosan nanomagnetic composite material, with cumulative adsorption surface area for the simultaneous adsorption of Cu (II) and Zn (II) ions. The physicochemical properties of both treated and untreated forms of the adsorbent were

Table 1
Physiochemical properties of the adsorbents.

Parameters	KOH Treated guava leaves	Untreated guava leaves
pH	7.8	5.7
EC (μS/cm)	884	478
Moisture Content (%)	5	10.7
Bulk density (g/cm^3)	0.3	0.6
Total acidity (mol/g)	4750	4900
Total basicity (mol/g)	725	250
Decolourizing agent	9	6
Ion exchange capacity	0.21	0.16
Ash content (%)	5.6	16.8
pH_{zpc}	8	5
Total acid group (meq/g)	3.96	5.72
Total basic group (meq/g)	8.65	4.9
Carboxyl group (meq/g)	0.97	1.6
Lactone group (meq/g)	0.26	0.54
Phenolic group (meq/g)	3.05	4.1
BET Surface Area (m^2/g)	308.43	96.33

given in Table 1. The above parameters showed that KOH-treated adsorbent had better efficiency than untreated as well as with other agents like NaOH, $ZnCl_2$ etc. Maximum adsorption capacity of zinc onto NaOH – treated rice husk was 20.1 mg/g [20] and for $ZnCl_2$-treated sunflower seed husks, the maximum adsorption for Zn (II) was 19.8 mg/g [21].

Regarding physicochemical properties, the moisture content of the adsorbent in its H^+ state was determined to be 5%. This observation signifies a highly favourable outcome for the treated adsorbent, displaying notably lower moisture levels when contrasted with an unknown sample (10.78%) as noted by Ozdemir et al. [22]. The reduced moisture content is attributed to a significant degree of cross-linking within the treated material. Furthermore, the treated adsorbent exhibited an ion exchange capacity of 0.21 m^2/g, a characteristic possibly attributed to the substantial volume of micro-pores present, as identified by Hamid et al. [23]. Surface functional groups of the adsorbent were subjected to analysis using Boehm's titration, confirming the presence of basic groups on the adsorbent's surface, as previously established by Wang et al. [24]. The utilization of SEM analysis provided insights into the surface features of the adsorbent material. Notably, the SEM images at 100X and 200X magnification for both treated and untreated materials are depicted in Fig. 1, facilitating a comprehensive understanding of their respective surface characteristics. The SEM image of the treated guava leaves appears more comb like structure, the fragmented configuration of the material showed a state of transition between the amorphous and crystalline phases [25]. The adsorbent exhibits a diverse array of irregular pores, varying in size and shape, resulting in a substantial accessible surface area conducive to the adsorption of heavy metals [26]. Thus, the SEM images of the material shows a significant crystalline segment with a small number of voids.

The XRD plate of the material is exhibited in Fig. 2. This configuration exhibited a prominent characteristic peak accompanied by a broad shoulder. The assessment of the relative half-width value (theta value) substantiated the crystalline nature of the broad peaks observed in the guava leaves [27,28]. The FTIR spectrum of the treated adsorbent is measured using a reference KBR pellet medium. The groups and the band frequencies are designating for the adsorbent are based on earlier literature. In Fig. 3 and Table S1, the emergence of the peak at 3400 cm^{-1} is indicative of OH elongation. The bands observed at 2922 cm^{-1} are associated with symmetric C—H expansion. Notably, the appearance of the peak at 2359 cm^{-1} corresponds to intense stretching vibrations of O=C=O. Additionally, the presence of the band at 1580 cm^{-1} signifies the asymmetric vibration of COO^-. The contribution from both O—H bending modes and C—O stretching of phenolic groups is reflected by the band at 1153 cm^{-1} [28].

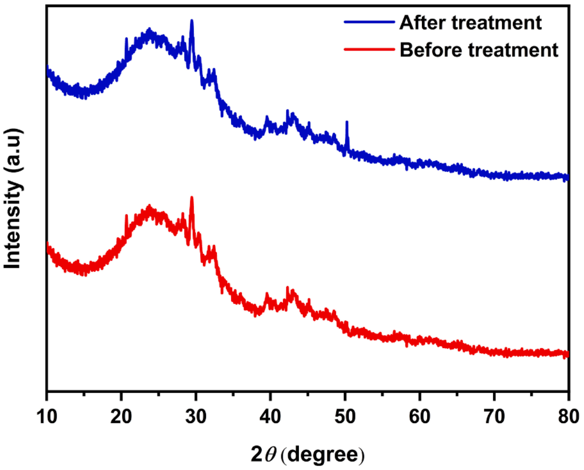

Fig. 2. The XRD images of the KOH treated guava leaves (a) before treatment, (b) after treatment.

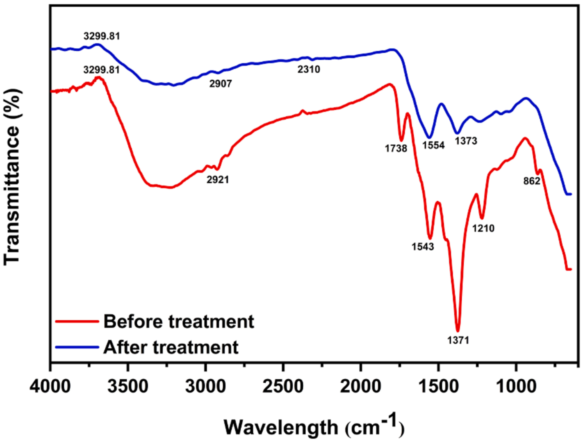

Fig. 3. FTIR Spectrum of the KOH treated guava leaves before and after adsorption.

3.2. Separation studies by batch

The adsorbent ion exchange capacity was studied by employing the batch equilibrium method for Zn (II) ions. Ion exchange investigations were conducted under varied experimental parameters such as diverse

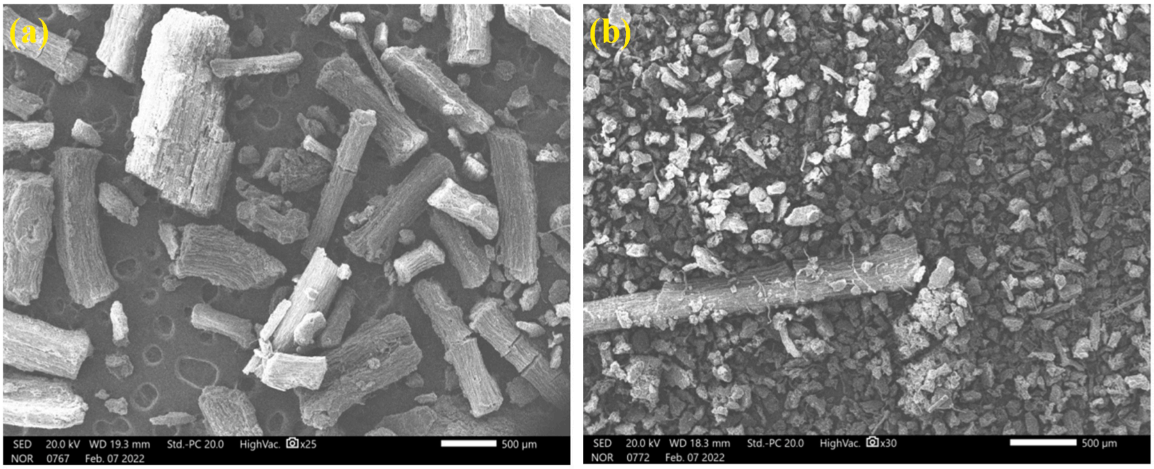

Fig. 1. The SEM Pictures of KOH treated guava leaves (a) before treatment, (b) after treatment.

dosage, concentration, temperature, time intervals, pH and desorption to authenticate the efficiency and feasibility of the adsorbent.

3.3. *Study of initial concentration as well as equilibrium time*

The uptake rate of Zn (II) ions was evaluated at various concentrations (5, 10, 20, 30, and 40 mg/L) (Figure S1), The results indicated that the timeframe for achieving higher uptake, ranging from 2.1 to 10.1 mg/g of Zn (II) ions, was 2 h (equilibrium state reached at 30 and 40 min). The nano porous nature of the adsorbent's surface, as confirmed by SEM analysis, contributes to its efficient adsorption process. Notably, the maximum adsorption capacity of KOH treated guava leaves was measured at 14.5 mg/g (as depicted in Table 2), underscoring their effectiveness as a valuable adsorbent in the market. Table 3 shows a comparison of adsorption capacity for zinc ions with another adsorbent.

Kinetic models for the adsorption study were examined using first order [31] and second order kinetics. Comparing the empirical data (q_e) with the calculated values (q_e) from the second order model plots, in conjunction with the analysis of the Lagergren kinetic plots (Table 4), demonstrated a closer alignment. The calculated correlation values further reinforced the unity for the second-order kinetic model. Hence, the adsorption kinetics for Zn (II) ions exhibited a favorable agreement with the second-order kinetic study. This similarity was also observed in the adsorption of Zn (II) onto *Colocasia esculenta* [32].

3.4. *Dose study*

The study examined the Zn (II) removal using KOH treated guava leaves at varying doses ranging from 100 to 700 mg/50 mL for zinc concentrations of 10 to 40 mg/L. The investigation revealed that an increase in adsorbent dose corresponded to an elevated Zn (II) ion removal, with complete removal occurring at doses of 200, 300, 400 per 50 mL for concentrations of 10, 20, 30, and 40 mg/L, respectively (Figure S2). This observed trend can be attributed to the heightened availability of adsorption sites and the increased surface area of the adsorbent at higher doses [33]. The abundant adsorption sites on the KOH treated guava leaves facilitate more extensive interactions with Zn (II) ions, resulting in enhanced removal efficiency. Therefore, adjusting the adsorbent dose can play a crucial role in optimizing the removal of Zn (II) ions from the aqueous solution, offering a potential approach for efficient and sustainable water treatment [34].

3.5. *Effect of pH on adsorption*

The impact of pH was systematically explored across an initial pH range of 2 to 12, using initial Zn (II) concentrations of 20 and 30 mg/dm^3. Optimal Zn (II) removal occurred within the pH range of 3 to 10. Conversely, zinc removal was least effective at pH levels below 3 and above 10 (Fig. 4A). The reduced adsorption below pH 4 can be attributed to potential Cl-ion competition, particularly when hydrochloric acid is externally added to regulate pH, leading to foreign ion effects. Above pH 8, the decline in adsorption is attributed to OH- ion competition with Zn (II) ions. The removal process involves successive ion exchange, facilitated by the KOH treated adsorbent, as evidenced by the study by Namasivayam and Subha [27]. As the pH increased from 8 to 11, the protonation degree of carbon surfaces diminished, resulting in lowered removal due to electrostatic repulsion. Notably, highly negatively charged adsorbents with a markedly basic pH exhibit less favorable adsorption, primarily due to electrostatic repulsion between anions and the negatively charged adsorbent surface.

Table 2
Isotherm models for the adsorption of Zn (II) on to KOH treated guava leaves.

Model	Parameter	Zinc (Zn^{+2})
Langmuir	Q_o (mg/g)	14.5
	b (L/mg)	0.08
	R^2	0.97
Freundlich model	K_f (mg/g (L/mg)$^{1/n}$)	1.15
	N	1.3
	R^2	0.98
Dubinin-Radushkevich model	q_m (mg/g)	923.9
	E (kJ/mol)	70
	R^2	0.92
Temkin	A (L/mg)	1
	B (mg/g)	0.12
	R^2	0.20

Table 3
Comparison of adsorption capacity for Zn ions with other adsorbent.

Adsorbent	Adsorption capacity	References
Jatropha curcas L.	14.8 mg/g	[11]
Albizia zygia	17.2 mg/g	[29]
Alginate immobilized *Pencillium* sp.	3.7 mg/g	[16]
Goethite	1.1 mg/g	[30]
KOH treated guava leaves	14.5 mg/g	At this work

Collectively, this investigation underscores the pivotal role of pH in Zn (II) adsorption when utilizing the KOH treated adsorbent, with the optimal pH range identified as 3 to 10 for highly effective Zn (II) removal. Additionally, it sheds light on the significant contributions of ion exchange and electrostatic interactions, thus enhancing our comprehensive comprehension of the multifaceted adsorption mechanisms governing Zn (II) adsorption onto the selected adsorbent [34,35].

3.6. *pH study on desorption*

In order to build the adsorption process much more economical, it is compulsory to regenerate the spent material and adsorbate. Maximum desorption of 46 and 66% occurred with pH 12, for 20 and 30 mg/L concentrations of Zn (II) in this study, respectively. pH ranging from 4 to 11 desorption was found to be $<$ 12% for studied concentrations of Zn (II) (Fig. 4B). As the pH increased, the investigation into desorption correspondingly reflected an escalation in OH^- concentration. The pH and desorption effect results revealed that the mechanism of ion exchange is effective in the treatment by adsorption. About a complete desorbing of Zn (II) from metal-laden adsorbent at pH 12 confirming the mechanisms exchange. By understanding and optimizing the desorption process, this research contributes to making the overall adsorption process more sustainable and cost-effective. The capacity for successful regeneration of the adsorbent material and subsequent retrieval of adsorbed metal ions under higher pH conditions offers significant insights into the potential real-world utility of guava leaves as an environmentally friendly and efficient adsorbent for heavy metal elimination [36–38].

3.7. *Evaluation of zn (II) ions uptake capacity in the presence of other metal ions*

The exploration encompassed an examination of the impact of Cd (II), Cu (II), and Zn (II) ions at varying concentrations under conditions of equilibrium during the interaction with the metal adsorbent. A perusal of the Fig. 5 reveals that the amount of Zn (II) ions uptake by the adsorbent material has no change in equilibrium time and residual concentration in the presence of other ions [25].

3.8. *Regeneration of the adsorbent/adsorbate*

While ensuring an adsorbent's reusability is crucial to minimize treatment costs and manage used adsorbents, restoring the uptake capacity of an adsorbent containing robust adsorption sites through desorption remains challenging. In the second cycle, the Langmuir adsorption capacity of KOH treated guava leaves was observed to remain consistent with the first cycle under identical experimental

Table 4

Kinetic model constant values for Zn (II) adsorption by KOH treated guava leaves.

Parameter	qe (exp) mg/g	First order model			Second order model			Elovich Model		
Conc. in (mg/L)		k_1 (/min)	q_e cal (mg/g)	R^2	k_2 (g/mg/min)	q_e cal (mg/g)	R^2	α (mg/g/min)	β (g/mg)	R^2
5	1	0.11	0.5	0.99	0.26	1.08	0.9	0.8	4.5	0.91
10	2	0.12	0.9	0.99	0.22	2.19	1	7.9	3.1	0.98
20	3.9	0.13	2.3	0.99	0.08	4.26	1	5.9	1.4	0.99
30	5.6	0.15	2.7	0.99	0.08	4.26	0.9	5.4	1.3	0.99
40	7	0.11	2.9	0.97	0.05	5.32	0.9	4.4	0.9	0.97

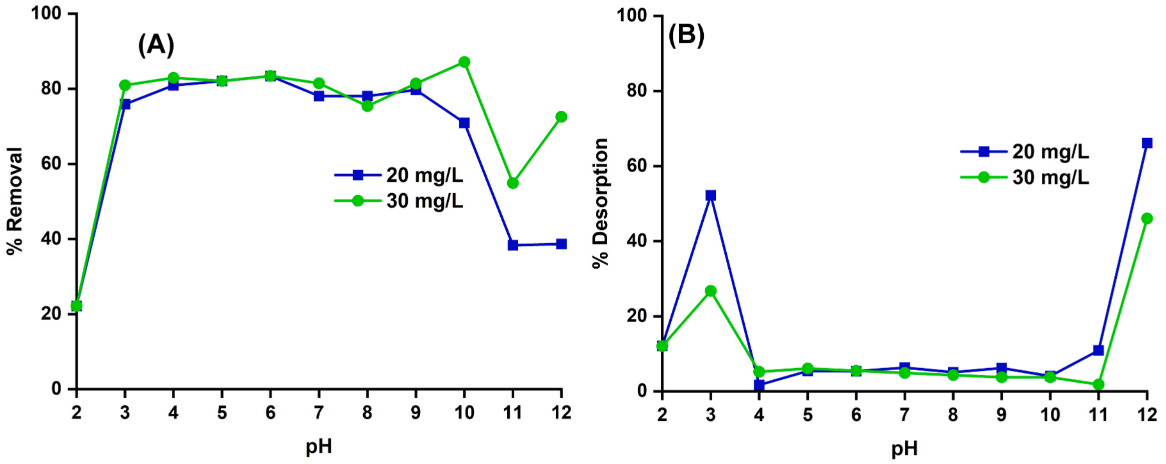

Fig. 4. pH effect on (A) adsorption and (B) desorption of zinc.

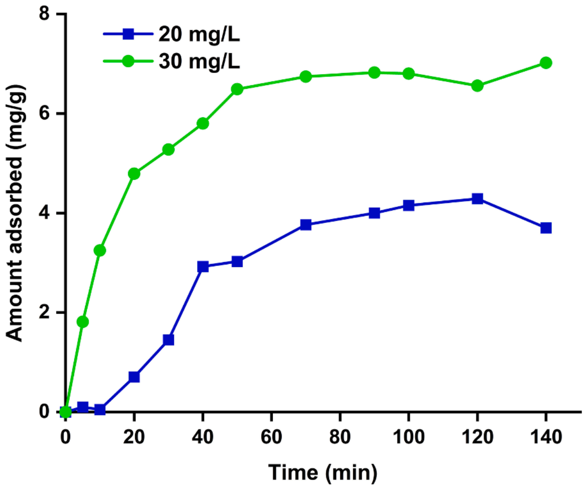

Fig. 5. Effect of contact time with other metal ions.

conditions (Fig. S3). A significant decrease in adsorption capacity in the second cycle compared with first cycle adsorption may be due to fracturing of pores and thinning of the walls of the pores during the first cycle and recovery process. In a similar manner, the entire process was repeated for the 3rd, 4th and 5th cycles respectively. The result revealed the spent material is suitable for regeneration [23].

3.9. Practical applications

The findings of this research have significant practical implications for water treatment and environmental management. The efficient removal of zinc ions from synthetic wastewater using KOH-treated guava leaves can be directly applied to industrial and municipal wastewater treatment processes, which are in eco-friendly adsorbent offers a cost-effective and sustainable solution for reducing heavy metal contamination in water sources. The application of guava leaves in environmental remediation projects can address heavy metal pollution in soil and water bodies. This method can aid in restoring ecosystems impacted by heavy metal contamination and contribute to cleaner environments. Furthermore, regions with limited access to advanced water purification technologies, the use of guava leaves as an adsorbent can provide an accessible and affordable means of purifying drinking water, especially in communities at risk of heavy metal exposure. Also, industries generating wastewater with heavy metal content can incorporate guava leaf adsorption as a pre-treatment step before discharging effluents. This can help them meet environmental regulations and minimize the environmental footprint of their operations.

3.10. Future research prospects

The success of this research paves the way for several intriguing avenues of future investigation. Such as, multi-metal adsorption as expanding the scope to investigate the efficacy of KOH-treated guava leaves in removing a broader range of heavy metals beyond zinc, such as lead, copper, and cadmium. Further research can focus on optimizing the production process and scaling up the use of guava leaves for industrial applications, ensuring cost-effectiveness on a larger scale. Developing sustainable methods for regenerating and reusing guava leaves as adsorbents to enhance their long-term utility in wastewater treatment.

Also, conducting field studies to assess the practical applicability and challenges of guava leaf-based adsorption in real-world environments, considering factors such as pH, temperature, and competing ions. Investigating the environmental impact of using guava leaves as an adsorbent in terms of sustainability, spent adsorbent disposal, and potential ecological consequences. Furthermore, involved in developing theoretical models to predict the adsorption behaviour of guava leaves under different conditions, aiding in the design of optimal treatment processes. In summary, the research on KOH-treated guava leaves as an eco-friendly adsorbent not only contributes to the field of wastewater treatment but also offers a sustainable solution for addressing water pollution and heavy metal contamination. The practical applications and future research prospects outlined here underscore the versatile and promising nature of this eco-friendly adsorbent.

4. Conclusions

In conclusion, this research paper investigated the potential of KOH treated guava leaves as an adsorbent for removing zinc ions from aqueous solutions. The SEM images provided evidence of textural modifications in KOH treated guava leaves, supporting their efficiency as an adsorbent. The investigation revealed an escalating percentage of removal as the adsorbent doses increased, while the recuperative desorption rate post adsorption indicated its potential applicability in adsorption flows. The outcomes underscore the economic and efficient attributes of KOH treated guava leaves as an adsorbent for zinc ion removal from wastewater. The Freundlich isotherm model aptly depicted the equilibrium data, disclosing a peak monolayer adsorbent capacity of 14.5 mg/g for Zn (II) ions within defined optimal conditions. Moreover, the pseudo-second-order kinetic model exhibited discernible selective adsorption kinetics. Overall, the significance of KOH treated guava leaves as a sustainable solution for addressing heavy metal contamination in water sources is emphasized. The findings contribute to the growing body of knowledge in the field of eco-friendly adsorbents for wastewater treatment.

5. Data availability statement

The data presented in this study are available on request from the corresponding authors.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

This work was supported by DST-SERB (EEQ), New Delhi (Ref. No. EEQ/2019/000184), under the EMEQ project. All the authors are thankful to their respective universities and institutes for their support.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jtice.2023.105283.

References

[1] Bohli T, Ouederni A, Fiol N, Villaescusa I. Single and binary adsorption of some heavy metal ions from aqueous solutions by activated carbon derived from olive stones. Desalin Water Treat 2013:1–7. https://doi.org/10.1080/19443994.2013.859099.

[2] Zwain HM, Vakili M, Dahlan I. Waste material adsorbents for zinc removal from wastewater: a comprehensive review. Inter J Chem Eng 2014;2014:1–13. https://doi.org/10.1155/2014/347912.

[3] Prasanna Kumar P, Prasanna Kumar Y, Venkateswara RB. Optimization of Zinc (II) biosorption on to *Boodlea struveiodes* (marine algae) by central composite design. Rasayan J Chem 2017;10:1025–36. https://doi.org/10.7324/RJC.2017.1031683.

[4] Nsami NJ, Daouda K, Mbadcam JK. Adsorption of Zinc(II) ions from aqueous solution onto kaolinite and metakaolinite. Der Pharma Chemica 2015;7:51–8.

[5] Chon K, Kim Y, Bae DH, Cho J. Confirming anthropogenic influences on the major organic and inorganic constituents of rainwater in an urban area. Drink Water Eng Sci 2015;8:35–48. https://doi.org/10.5194/dwes-8-35-2015.

[6] Omrani M, Ruban V, Ruban G, Lamprea K. Assessment of atmospheric trace metal deposition in urban environments using direct and indirect measurement methodology and contributions from wet and dry depositions. Atmos Environ 2017;168:101–11. https://doi.org/10.1016/j.atmosenv.2017.08.064.

[7] WHO. Adverse health effects of heavy metals in children. WHO 2011. apps.who.int/iris/handle/10665/336875 (accessed August 8, 2023).

[8] Atangana E. Adsorption of Zn (II) and Pb (II) ions from aqueous solution using chitosan cross-linked formaldehyde adsorbent to protect the environment. J Polym Environ 2019;27:2281–91. https://doi.org/10.1007/s10924-019-01523-x.

[9] WHO. Pesticides used for vector control in drinking-water sources and containers. WHO 2008:482–3. cdn.who.int/media/docs/default-source/wash-documents/water-safety-and-quality/chemical-fact-sheets-2022/bacillus-thuringensis-israelensis-fact-sheet-2022.pdf?sfvrsn=f73cfc7f_2&download=true.

[10] Fu F, Wang Q. Removal of heavy metal ions from wastewaters: a review. J Environ Manage 2011;92:407–18. https://doi.org/10.1016/j.jenvman.2010.11.011.

[11] Nacke H, Gonçalves AC, Campagnolo MA, Coelho GF, Schwantes D, dos Santos MG, et al. Adsorption of Cu (II) and Zn (II) from water by *Jatropha curcas* L. as biosorbent. Open Chem 2016;14:103–17. https://doi.org/10.1515/chem-2016-0010.

[12] Rajczykowski K, Sałasińska O, Loska K. Zinc removal from the aqueous solutions by the chemically modified biosorbents. Water Air Soil Pollut 2018;229:6. https://doi.org/10.1007/s11270-017-3661-5.

[13] Deng H, Li Q, Huang M, Li A, Zhang J, Li Y, et al. Removal of Zn (II), Mn (II) and Cu (II) by adsorption onto banana stalk biochar: adsorption process and mechanisms. Water Sci Technol 2020;82:2962–74. https://doi.org/10.2166/wst.2020.543.

[14] Tan Peng Jun P, Wan Osman WNA, Samsuri S, Md Saad J, Samsudin MF. Hernández Yáñez E. Factory tea waste biosorbent for Cu (II) and Zn (II) removal from wastewater. E3S Web Conf 2021;287:04006. https://doi.org/10.1051/e3sconf/202128704006.

[15] Michael Ogunjobi K, Jayeola VA, Friday Gakenou O, Oluwaseun Olufemi O, Oluwafemi Ayanleye S, Jumoke Lawal K. Biosorption potentials of sawdust in removing zinc ions from aqueous solution. IJSRM 2021;9:191–8. https://doi.org/10.18535/ijsrm/v9i10.fe01.

[16] DO J, Uzairu A, Ekwumemgbo P. Biosorption of zinc from aqueous solution by *Penicillium* Sp Immobilised in calcium alginate. Sci World J 2019;14:2019.

[17] Ugwu EI, Agunwamba JC. Optimal conditions for adsorption of zinc from industrial wastewater using groundnut husk ash. Environ Monit Assess 2020;192:345. https://doi.org/10.1007/s10661-020-08262-w.

[18] Ofomaja AE, Naidoo EB, Modise SJ. Biosorption of copper (II) and lead (II) onto potassium hydroxide treated pine cone powder. J Environ Manage 2010;91:1674–85. https://doi.org/10.1016/j.jenvman.2010.03.005.

[19] Pooladi A, Bazargan-Lari R. Simultaneous removal of copper and zinc ions by chitosan/hydroxyapatite/nano-magnetite composite. J Mater Res Technol 2020;9:14841–52. https://doi.org/10.1016/j.jmrt.2020.10.057.

[20] Zhang Y, Zheng R, Zhao J, Zhang Y, Wong P, Ma F. Biosorption of zinc from aqueous solution using chemically treated rice husk. Biomed Res Int 2013;2013:1–7. https://doi.org/10.1155/2013/365163.

[21] Srisorrachatr S. Modified sunflower seed husks for metal ions removal from wastewater. Chem Eng Trans 2017;57:247–52. https://doi.org/10.3303/CET1757042.

[22] Ozdemir S, Turp SM, Oz N. Simultaneous dry-sorption of heavy metals by porous adsorbents during sludge composting. Environ Eng Res 2020;25:258–65. https://doi.org/10.4491/eer.2019.071.

[23] Hamid AA, Alam J, Shukla AK, Ali FAA, Alhoshan M. Sustainable removal of phenol from wastewater using a biopolymer hydrogel adsorbent comprising crosslinked chitosan and κ-carrageenan. Int J Biol Macromol 2023;251:126340. https://doi.org/10.1016/j.ijbiomac.2023.126340.

[24] Wang W, Pan Q, Wang R, Ge T. Modeling and optimization of a honeycombed adsorbent bed for efficient moisture capture. Appl Therm Eng 2022;200:117717. https://doi.org/10.1016/j.applthermaleng.2021.117717.

[25] Azarudeen RS, Subha R, Jeyakumar D, Burkanudeen AR. Batch separation studies for the removal of heavy metal ions using a chelating terpolymer: synthesis, characterization and isotherm models. Sep Purif Technol 2013;116:366–77. https://doi.org/10.1016/j.seppur.2013.05.043.

[26] Durairaj K, Senthilkumar P, Velmurugan P, Divyabharathi S, Kavitha D. Development of activated carbon from *Nerium oleander* flower and their rapid adsorption of direct and reactive dyes. Int J Green Energy 2019;16:573–82. https://doi.org/10.1080/15435075.2019.1598419.

[27] Namasivayam C, Subha R. Kinetics and isotherm studies for the adsorption of phenol using low cost micro porous $ZnCl_2$ activated coir pith carbon. J Environ Eng Sci 2013;8:23–35. https://doi.org/10.1680/jees.2013.0003.

[28] Durairaj K, Senthilkumar P, Priya V, Velmurugan P, Jagadeesh Kumar A. Novel synthesis of *Chrysanthemum indicum* flower as an adsorbent for the removal of direct congo red from aqueous solution. Desalin Water Treat 2018;113:270–80. https://doi.org/10.5004/dwt.2018.22292.

[29] Chimezie E. Effects of *Albizia zygia* charcoal on the growth and performance of maize (*Zea mays* L.). EJPAS 2016;4:1–9. www.idpublications.org/wp-content/uploads/2016/03/Full-Paper-EFFECTS-OF-ALBIZIA-ZYGIA-CHARCOAL-ON-THE-GROWTH-AND-PERFORMANCE.pdf.

[30] Dash B, Dash B, Rath SS. A thorough understanding of the adsorption of Ni (II), Cd (II) and Zn (II) on goethite using experiments and molecular dynamics simulation. Sep Purif Technol 2020;240:116649. https://doi.org/10.1016/j.seppur.2020.116649.

[31] Khan MdM-U-R. Analytical solution of van der pol's differential equation using homotopy perturbation method. J Appl Math Phys 2019;07:1–12. https://doi.org/10.4236/jamp.2019.71001.

[32] Maity S, Nanda S, Sarkar A. *Colocasia esculenta* stem as novel biosorbent for potentially toxic metals removal from aqueous system. Environ Sci Pollut Res 2021;28:58885–901. https://doi.org/10.1007/s11356-021-13026-1.

[33] Kaliannan D, Palaninaicker S, Palanivel V, Mahadeo MA, Ravindra BN, Jae-Jin S. A novel approach to preparation of nano-adsorbent from agricultural wastes (*Saccharum officinarum* leaves) and its environmental application. Environ Sci Pollut Res 2019;26:5305–14. https://doi.org/10.1007/s11356-018-3734-z.

[34] Li J, Wu Z, Duan Q, Li X, Li Y, Alsulami H, et al. Simultaneous removal of U (VI) and *Re* (VII) by highly efficient functionalized ZIF-8 nanosheets adsorbent. J Hazard Mater 2020;393:122398. https://doi.org/10.1016/j.jhazmat.2020.122398.

[35] Mohamad Yusop MF, Mohd Johan Jaya E, Ahmad MA. Single-stage microwave assisted coconut shell based activated carbon for removal of Zn (II) ions from aqueous solution – optimization and batch studies. Arab J Chem 2022;15:104011. https://doi.org/10.1016/j.arabjc.2022.104011.

[36] Guerrero-Fajardo C, Giraldo L, Moreno-Piraján J. Preparation and characterization of graphene oxide for Pb (II) and Zn (II) ions adsorption from aqueous solution: experimental, thermodynamic and kinetic study. Nanomater 2020;10:1022. https://doi.org/10.3390/nano10061022.

[37] Narindri Rara Winayu B, Ho JY, Hsueh HT, Chu H. Multifunctional *Thermosynechococcus* sp. CL-1 cultivation in swine wastewater for nutrients utilization, CO_2 fixation, and C-phycocyanin production. J Taiwan Inst Chem Eng 2023:105046. https://doi.org/10.1016/j.jtice.2023.105046.

[38] Natarajan B, Kannan P, Rather JA, Sheikh RA. Recent developments in metal nanoparticles functionalized nanocomposite adsorbents for heavy metals removal from wastewaters. J Taiwan Inst Chem Eng 2023;147:104942. https://doi.org/10.1016/j.jtice.2023.104942.